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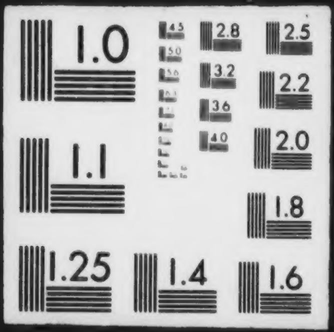
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ASSESSMENT OF CATALYSTS FOR CONTROL OF NOx FROM STATIONARY POWER PLANTS, PHASE 1, VOLUME I

TRW SYSTEMS

PREPARED FOR
ENVIRONMENTAL PROTECTION AGENCY

JANUARY 1975

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ASSESSMENT OF CATALYSTS FOR CONTROL OF NO_X FROM STATIONARY POWER PLANTS, PHASE 1 VOLUME I - FINAL REPORT

by

E.P. Koutsoukos, J.L. Blumenthal,
M. Ghassemi (TRW), and G. Bauerle (UCLA)

TRW Systems Group
One Space Park
Redondo Beach, California 90278

Contract No. 68-02-0648
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EPA Project Officer: J.B. Wingo

Control Systems Laboratory
National Environmental Research Center
Research Triangle Park, North Carolina 27711

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ABSTRACT

This two volume document summarizes the investigations performed by TRW and the UCLA School of Engineering and Applied Sciences on the technical and economic feasibility of catalysts for nitrogen oxide control from power generating plants. The objective of the program was to assess the potential of utilizing catalytic processes in power plant nitrogen oxide emission abatement.

The approach taken to meet the objective involve a literature survey and the development of a data bank on pertinent articles and patents, experimental screening tests on selected promising catalysts, and preliminary design and cost analyses on candidate processes adapted to new and/or existing power plants.

The stepwise selection and prioritization of catalysts led to the conclusion that at least two types of catalytic nitrogen oxide control processes should be adaptable to power generating plants. These are: selective reduction of nitrogen oxides with ammonia on non-noble metal catalysts and simultaneous nonselective reduction of nitrogen and sulfur oxides with coal derived reductants on non-noble metal catalysts.

Volume I of this report presents our assessment and conclusions. Volume II is comprised of three data bank citation indices.

This report is submitted in fulfillment of Contract No. 68-02-0648 under the sponsorship of the Environmental Protection Agency. Work was completed in in May 1974.

CONTENTS

Page

Abstract iii

List of Figures vii

List of Tables ix

Acknowledgements xii

Conclusions xiii

Recommendations xv

Sections

1. Introduction 1

2. Nature of the Problem and Approaches to Its Solution 5

3. Development of a Data Bank on NO_x Catalysts and Catalytic Processes (Task 1) 15

    3.1 Catalytic NO_x Decomposition 18

    3.2 Selective Catalytic Reduction of NO_x 36

    3.3 Nonselective Catalytic Reduction of NO - Simultaneous NO_x-SO_x Abatement 68

    3.4 Catalytic Oxidation of Nitric Oxide 89

    3.5 Task 1 Conclusions and Candidate Catalyst Selection 92

    3.6 Potential Hazardous Products of Catalytic NO_x Abatement Schemes 96

4. Catalyst Screening and Proof-of-Principle Experiments (Task 2) 105

    4.1 Catalysts Selected for Screening 105

    4.2 Catalyst Preparation 109

    4.3 Catalysts Screening Test Conditions 114

    4.4 Catalyst Screening Test Results 120

    4.5 Parametric Investigations on Platinum, Vanadia, and Iron-Chromium Oxide Catalysts 144

    4.6 Prioritized Listing of NO_x Abatement Catalysts Based on Task 2 Investigations 174

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CONTENTS (CONTINUED)

Page

5. Evaluation of the Cost Effectiveness in the Use of Catalysts to Reduce NO_x Emissions from Power Plants (Task 3) 177

5.1 Preliminary Design and Cost Analysis of Simultaneous NO_x-SO_x Reduction Schemes 179

5.2 Preliminary Design and Cost Analysis of Selective NO_x Reduction with Ammonia Schemes 202

5.3 Summary of Preliminary Design and Cost Analysis Results on Five NO_x Abatement Schemes Adapted to 800 MW Power Plants 208

6. Recommendations for Further Action (Task 4) 215

APPENDICES 223

Appendix A 225

Appendix B 237

FIGURES

No. Page

1 Equilibrium Chemical Composition of CH_4-Air Flames as a Function of Mixture Ratio 7

2 Adiabatic Flame Temperature as a Function of Oxidizer-Fuel Mixture Ratio for Methane-Air Flames 7

3 Decomposition of NO on Pt Catalysts 35

4 Reduction of NO and O_2 on Fe_2O_3 as a Function of Temperature 41

5 Selective NO_x Reduction by NH_3 on Pt as a Function of Temperature and Space Velocity 49

6 Selective NO_x Reduction by NH_3 on Pt as a Function of NH_3/NO and Space Velocity 49

7 Reduction of NO with NH_3 on Fe-Cr Catalyst at 400°C, 14% CO, 5% H_2O, 3% O_2 Present in N_2 Carrier 59

8 Effect of Temperature on Selective NO Reduction by NH_3; Fe-Cr Oxide Mixture Catalysts 61

9 Reduction of NO with NH_3 on V_2O_5 Catalyst at 400°C, 14% CO_2 5% H_2O, 3% O_2 Present in N_2 Carrier 63

10 Temperature and Oxygen Effect on Selective NO Reduction by Ammonia; Vanadia Catalysts 65

11 Reduction of NO with NH_3 on Pt Catalysts, 250°C, Synthetic Flue Gas (14% CO_2, 5% H_2O, 3% O_2 in N_2). 67

12 COS Production as a Function of SO_2 Reduction on CuO Catalyst 77

13 Residual Sulfur Species in Flue Gas Reduced on CuO Versus Extent of SO_2 Reduction 77

14 TRW Simultaneous Catalytic NO_x-SO_x Reduction by Coal Process 79

15 NO_x-SO_x Abatement by the Chevron Hitachi Process 85

16 NO_x-SO_x Abatement by the TRW Sulfide Process 87

17 Continuous Catalytic NO_x Absorption Process 91

18 TRW "OXNOX" Oxidative Scrubbing Process 93

19 Catalyst Screening Test Apparatus 115

20 Decomposition of NO on Pt Catalyst (NA-2) 149

FIGURES (CONTINUED)

No.		Page
21	Reduction of NO with NH_3 on Pt Catalyst at 250°C (14% CO_2, 5% H_2O, 3% O_2 in N_2)	157
22	Effect of O_2 Concentration and Temperature on NO Reduction with NH_3 on V_2O_5 Catalyst (Harshaw)	159
23	Reduction of NO With NH_3 on V_2O_5 Catslyst at 400°C (14% CO_2, 5% H_2O, 3% O_2 in N_2)	165
24	Reduction of NO with NH_3 on Fe-Cr Catalysts at 400°C (14% CO_2, 5% H_2O, 3% O_2 in N_2)	173
25	NO_x-SO_x Catalytic Reduction Process Adapted to New Power Plants (800 MW)	183
26	Monsanto's Multi-Section Catalytic Reactor	191
27	NO_x-SO_x Catalytic Reduction Process Adapted to Existing Power Plants (800 MW)	195
28	Sulfide Process Adaptation to an 800 MW Power Plant	199
29	NO_x Reduction with Ammonia Scheme (Non-Noble Metal Catalyst)	205
30	NO_x Reduction with Ammonia Scheme-Platinum Catalyst	209

TABLES

No. Page

1 Equilibrium Concentration of Nitric Oxide which can Form From a Starting Mixture of 80 Vol. % N_2, 10 Vol. % O_2, and 10 Vol. % He as a Function of Temperature 11

2. Keywords Used in Catalytic NO_x Document Control System 17

3 Results of IIRI's Study of Nitric Oxide Decomposition Catalysts-Commercial Catalysts 21

4 Results of IIRI's Study of Nitric Oxide Decomposition Catalysts-Laboratory Prepared Catalysts 23

5 Decomposition of NO at Low Concentrations 27

6 Summary of Task 2 Catalytic NO Decomposition and Oxidation Data 29

7 Decomposition of Nitric Oxide on Various Catalysts - Reaction Order with Respect to NO 33

8 Relative Effectiveness of Supported Catalysts for the CO-NO and $CO-O_2$ Reactions 39

9 Reduction of NO with H_2 on Catalysts PZ-1-168 (Supported Pt, UOP) in the Presence of Oxygen 42

10 Summary of Task 2 Data on Selective Reduction of NO with CO and H_2 45

11 Selective Treatment of Nitric Acid Plant Tail Gas 51

12 Published Data on Selective Reduction of NO with NH_3 in Simulated or Actual Flue Gas 55

13 Summary of Task 2 Data on Selective Reduction of NO with NH_3 57

14 Simultaneous Reduction of SO_2 and NO_x by Catalyzed Reaction with CO: Copper-on Al_2O_3 Catalyst, 538°C (1000°F), Reactants in N_2 71

15 Data on Reduction of SO_2 and NO by carbon Monoxide on Supported CuO 75

16 Typical Steady State Non-Optimized Results on TRW's NO_x-SO_x Catalytic Reduction Process 81

17 Catalytic NO_x-SO_x Reduction by CO on NYU Catalysts 83

TABLES (CONTINUED)

No.		Page
18	List of Catalysts Subjected to Screening Tests	107
19	Approximate Composition of Rare Earth Oxide Mixtures	111
20	Catalyst Screening Test Conditions	117
21	Results of Tests with Empty Reactor	119
22	Catalyst Screening Test Results (Pt and Pt-Mo Catalysts)	121
23	Catalyst Screening Test Results (Mo Based Catalysts)	125
24	Catalyst Screening Test Results (Rare-Earth Oxide Based Catalysts)	129
25	Catalyst Screening Test Results (Copper and Copper-Lead Catalysts)	133
26	Catalyst Screening Test Results (Tungsten Oxide and Vanadia Catalysts)	135
27	Catalyst Screening Test Results (Iron-Chromium Oxide Catalysts)	137
28	Catalyst Screening Test Results (Iron Oxide and Iron Graphite Catalysts)	143
29	Decomposition of NO on Pt Catalyst (NA-2)	147
30	Parametric Effects on Platinum Catalysts Used in the Selective Reduction of NO by NH_3	151
31	Temperature, Space Velocity and Short-Term SO_2 Effects on the Reduction of NO with NH_3 on Harshaw Vanadia (NA-25)	161
32	Effect of NO and NH_3 Concentration and Space Velocity on the Reduction of NO with NH_3 on Harshaw V_2O_5 Catalyst (NA-25)	163
33	Long-Term SO_2 Effect on the Catalystic Activity of Vanadia for the Selective NO-NH_3 Reaction	167
34	Parametric Investigations on Fe-Cr Oxide Cayalysts Employed in Selective Reduction of NO with NH_3	169
35	Reduction of NO with NH_3 on Fe-Cr Catalyst (NA-28) in the Presence of SO_2	171
36	Catalyst Ranking Based on Task 2 Data	175

TABLES (CONTINUED)

No.		Page
37	Assumed Chemical Composition for the Reductant Coal, Weight Percent	180
38	Assumed Power Plant Flue Gas Composition (Volume %)	181
39	Effect of Flue Gas Diversion Rate on Coal Feed Rates and Mass Balance Results	189
40	Breakdown of the Estimated Capital Cost for the NO_x-SO_x Catalytic Reduction Process for New Power Plants	193
41	Operating Cost Breakdown for the NO_x-SO_x Catalytic Reduction Process for New Power Plants	193
42	Breakdown of the Estimated Capital Cost for the NO_x-SO_x Catalytic Reduction Process for Existing Power Plants	197
43	Operating Cost Breakdown for the NO_x-SO_x Catalytic Reduction Process (Existing Power Plants)	197
44	Breakdown of Capital Cost for the Sulfide NO_x-SO_x Reduction Scheme for New Power Plants	201
45	Operating Cost Breakdown for the Sulfide NO_x-SO_x Reduction Scheme for New Power Plants	201
46	Breakdown of the Esitmated Capital Cost for NO_x Reduction by Ammonia Scheme - Non-Noble Metal Catalysts	207
47	Summary of the Breakdown of the Estimated Operating Cost for NO_x Reduction by Ammonia Scheme - Non-Noble Metal Catalysts	207
48	Breakdown of the Estimated Capital Cost for the NO_x Reduction by Ammonia Scheme - Platinum Catalysts	211
49	Breakdown of the Estimated Operating Cost for the NO_x Reduction by Ammonia Scheme - Platinum Catalysts	211
50	Capital and Operating Cost Estimates for the Adaptation of Catalytic NO_x and NO_x-SO_x Schemes to an 800 MW Power Plant - Summary Table	213

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CONCLUSIONS

The Phase I investigations on the "Technical and Economic Assessment of Catalysts for Control of NO_x from Stationary Power Plants" led to the following conclusions:

- Nitrogen oxide control from power plants by catalytic processes appears both technically and economically feasible on the basis of laboratory-scale data and preliminary engineering analysis.

- Two types of catalytic NO_x abatement processes exhibited the best potential for power plant adaptation: selective NO_x reduction with ammonia and nonselective simultaneous NO_x-SO_x reduction with coal derived reductants (CO and H_2). A nitric oxide decomposition on platinum process indicated promise for 50-60 percent NO_x abatement.

- Platinum based catalysts and a number of non-noble metal catalysts were identified as having medium to high activity in the promotion of the selective NO_x reduction with ammonia. The platinum on alumina catalysts indicated the highest activity in this process with an SO_2-free flue gas. An immediate and severe drop in platinum activity occurred as a result of sulfate deposition when a flue gas containing 1000 ppm SO_2 was used. The principle product of nitric oxide reduction with ammonia on platinum was N_2O. The active non-noble metal catalysts for the same reaction did not promote N_2O production (NO_x was reduced to nitrogen) and their activity was not affected by the presence of SO_2. Platinum was active in the 200-250°C range; non-noble metal catalysts indicated high activity in the 350-450°C range.

- The catalytic selective reduction of nitrogen oxides with ammonia appears to be a potential near term solution to the NO_x emission problem from existing power plants. Platinum based catalysts are indicated for utilization by power plants fired with sulfur free fuels. The high activity of these catalysts at relatively low temperatures facilitates the process adaptation to power plants. Non-noble metal catalysts, especially the iron-chromium oxide and vanadia catalysts, are the indicated promoters for the majority of existing power plants because of their resistance to SO_2 poisoning.
- The simultaneous nonselective NO_x-SO_x reduction schemes on non-noble metal catalysts are indicated as the desired approach to air pollution abatement for new power plants. Potentially, this approach represents the long term solution to NO_x-SO_x emissions from existing power plants.
- Catalysts for the selective reduction of nitrogen oxides by hydrogen or carbon monoxide were not identified.

Additional data is required before selection of the optimum NO_x abatement scheme for a particular type of power plant can be made.

RECOMMENDATIONS

As a result of the investigations performed under Phase I of this program, the TRW-UCLA Team recommends that the Phase I effort be followed by a second phase program which should concentrate on the bench-pilot scale development of the schemes identified in Phase I as promising candidates for NO_x and NO_x-SO_x abatement from power plants. Specifically, the team recommends the following technical effort:

- Engineering design data generation on the selective reduction of nitrogen oxides with ammonia on iron-chromium oxide catalysts. The product of this investigation should include empirical rate expressions for the process, as well as pilot or demonstration plant design curves; it should also include an assessment of the intermediate to long-term stability of catalytic activity under the conditions of intended use.

- Bench-scale development of the reductant generator to be used with either of two simultaneous NO_x-SO_x reduction processes identified as promising abatement schemes for power plant adaptation. This task should include engineering design data generation.

- Engineering design data generation on a single stage catalytic NO_x-SO_x reactor. The NYU catalyst is recommended as the prime candidate since proof-of-principle tests indicated that it does not promote COS and H_2S production. The task should include design data generation on the integrated reductant generator-catalytic reactor scheme.

- Bench-scale development of the catalytic-regenerative NO_x-SO_x reduction process (the Sulfide Process). The product of this effort should include complete scheme definition for new power plant adaptation, assessment of potential for existing plant adaptation, and adequate data for pilot plant design.

- Assessment of long-term platinum activity toward NO_x decomposition from SO_2 containing flue gases.

- Proof-of-principle investigations on a total pollutant abatement process recommended as a second generation air pollution abatement process for power plants. Prime candidate is the TRW "OXNOX" Process which in principle is capable of removing NO_x, SO_x, and trace elements from power plant flue gases through an oxidative wet scrubbing scheme.

The bench-scale scheme development tasks should include: (a) complete definition of reactor emissions and an assessment of their impact on the environment (even for nonregulated components); (b) proposed scheme impact on current pollution control equipment efficiency; and (c) capital, energy, and materials requirements and impact on supply if the scheme were to be universally adapted by power plants.

1. INTRODUCTION

The role of nitrogen oxides in smog formation and the hazardous effect of nitrogen dioxide to the respiratory system have been well documented and are virtually universally accepted. Whether present nitrogen oxide levels in the U.S. atmosphere as a whole warrant concern has been debated. Very few experts doubt, however, that if this air pollutant continues unabated its deleterious effects will be felt by a large portion of the U.S. and the world population in the future. Recent shortages in high grade (relatively clean) fuel availability and its high cost will bring future hazards nearer. Low grade fuels, with substantial nitrogen constituents, will soon be called upon to meet the worlds energy requirements. Proposed methods of combustion modification will have little effect on nitrogen oxide generation from the combustion of such fuels. Flue gas treatment appears to be the answer and the catalytic approach to flue gas treatment looks the most attractive in theory.

TRW in association with the UCLA School of Engineering and Applied Science were awarded by the Environmental Protection Agency a 15 month, two man-years program (Contract No. 68-02-0648) to assess the technical and economic feasibility of catalysts for NO_x control from power generating plants. The award represented Phase I of a two phase program aimed at identifying and testing one or more catalytic NO_x abatement processes suitable for power plant adaptation. Sufficient test and engineering analysis data were to be generated to permit pilot scale process design.

The objective of Phase I was to identify candidate catalytic NO_x abatement processes potentially suitable for power plant adaptation and to rank them in terms of technical feasibility and cost effectiveness. The approach taken to meet the objective involved a literature survey and the development of a data bank on pertinent articles and patents, catalyst screening tests on selected promising catalysts, and preliminary design and cost analyses on candidate processes adapted to new and/or existing power plants. Each step of this approach was aimed at the selection and prioritization of catalysts and catalytic process schemes in terms of their potential utilization in NO_x abatement from power plants.

The Phase I Program was divided into four tasks:

- Task 1 - Development of a Data Bank on NO_x Catalysts and Catalytic Processes involved the establishment of a data bank containing the latest state-of-the-art information on NO_x catalysts and catalytic processes. Data accumulation included: (a) a comprehensive review of TRW/UCLA's extensive in-house data on NO_x catalysts and catalytic processes dating back to 1955, (b) literature survey, (c) a review of current research grants and contracts in the field of NO_x control, and (d) interviews with officials of catalyst and carrier material manufacturing firms, of chemical, petroleum, and automotive industries, of electrical utilities, and of institutions and companies actively engaged in air pollution abatement research. The information and data obtained in the Task 1 effort was utilized to generate a list of candidate catalysts that indicated potential for use in the control of NO_x from stationary sources but had not yet been evaluated under representative flue gas conditions.

- Task 2 - Catalyst Screening and Proof-of-Principle Experiments involved the experimental evaluation of candidate catalysts selected in Task 1. These catalysts were evaluated on synthetic power plant flue gas and under conditions which closely simulated those of actual flue gases. Nitric oxide decomposition and/or oxidation catalysts, selective nitric oxide reduction catalysts, and nonselective NO_x-SO_x reduction catalysts were investigated. The highest ranked potential NO_x abatement catalysts were subjected to parametric scans in order to establish their sensitivity to variations in power plant flue gas conditions.

- Task 3 - Evaluation of the Cost Effectiveness of the Use of Catalysts to Reduce NO_x Emissions from Stationary Power Plants. Under this task a first level of detail process design and cost analysis was performed on NO_x abatement catalytic processes ranked highest as potential candidates for power plant adaptation as a result of Task 1 and Task 2 investigations.

- Task 4 - Recommendations for Further Action. This task summarizes the recommended further action on catalytic approaches to NO_x abatement from power plants. A research and development plan is outlined which indicates the sequence of tasks to be undertaken in the development of one or more catalytic NO_x abatement schemes to the demonstration level of testing. The recommendations are based on data developed in Tasks 1 through 3 of the Phase I Program.

The ensuing sections of this two volume report summarize the effort, results, conclusions, and recommendations of the Phase I Program on catalytic NO_x abatement from power plants.

2. NATURE OF THE PROBLEM AND APPROACHES TO ITS SOLUTION

It has been recognized for a number of years that oxides of nitrogen emanating primarily from high temperature combustion sources are a major reactant in the formation of photochemical smog. Nitric oxide (NO) which is formed in combustion processes usually converts in the atmosphere to the more hazardous nitrogen dioxide (NO_2). Concentrations of nitrogen dioxide as low as 10-20 ppm have been shown to cause persistent pathologic changes in animals. Thus, in addition to its role in the formation of photochemical smog, nitrogen dioxide, by itself, is a hazardous air pollutant. As our urban areas become larger it therefore becomes increasingly important to limit the emissions of oxides of nitrogen to the atmosphere.

Fossil fuel fired power plants represent the largest single stationary source of nitrogen oxide pollution in this country, accounting for approximately 23% of the total oxides of nitrogen emissions.[1] It is currently estimated that NO_x emissions from U.S. power plants total some 4.5 million tons per year.[1] Up to the present time the great majority of research and development on oxides of nitrogen pollution abatement (particularly in terms of catalytic abatement approaches) has been concentrated on the problem of mobile source emissions (estimated at 8 million tons/year) and relatively little work has been aimed directly at the distinctly different problem of controlling NO_x emissions from power plants. With the pending removal of lead from gasolines, technically viable approaches to controlling NO_x emissions from mobile sources appear to be at hand (although at current fuel prices the economic feasibility has been questioned). Analogous effort for NO_x abatement in stationary sources has been much less and, therefore, the required technology has not arrived.

Nitric oxide forms in high temperature flame environments through the direct combination of nitrogen and oxygen. In evaluating technical approaches for eliminating or removing oxides of nitrogen from fixed combustion sources, it is necessary to first consider the equilibrium thermochemistry involved. That is not to say that the chemical kinetics (both homogeneous and heterogeneous) are not of key importance, but equilibrium thermochemistry sets

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the limits on what can occur kinetically. Figures 1 and 2 show the adiabatic flame composition and temperature (at one atmosphere pressure) as a function of air-fuel ratio for a methane-air flame. From the thermochemical maps for the methane-air flame which are depicted in Figures 1 and 2 the following general observations can be drawn.*

- The maximum concentrations of nitric oxide which can form by nitrogen fixation in the methane-air flame occur at air-fuel ratios near to where maximum flame temperatures occur.

- The equilibrium chemical composition for fuel rich flames (air/ CH_4 wt. ratio <16) is considerably different from the flame composition for oxidizer rich flames (air/CH_4 wt. ratio >16). In particular, the carbon monoxide and hydrogen concentrations in the fuel rich flame are appreciable while the oxygen concentration is essentially zero. Just the opposite occurs in oxygen rich flames. The overall stoichiometry of fixed combustion sources (considering both the primary and secondary combustion zones) generally lies on the oxidizer rich side, and hence the combustion flue gases contain, in addition to NO, excess oxygen (3% typical) and essentially no reductants (CO and H_2). Therefore, in order to use a catalytic reduction process for removing nitric oxide (e.g., $2NO + 2CO \rightarrow N_2 + 2CO_2$), it is necessary to either grossly change the fuel to air ratio of current power boilers or add to the flue gas stream a particular reductant (e.g., NH_3) which will react selectively with NO.

- On the oxidizer rich side of Figure 1 where the concentrations of oxygen and nitrogen are essentially constant, the

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* These basic conclusions relative to nitrogen fixation are generally valid for coal and liquid hydrocarbon flames as well as for natural gas-air flames.

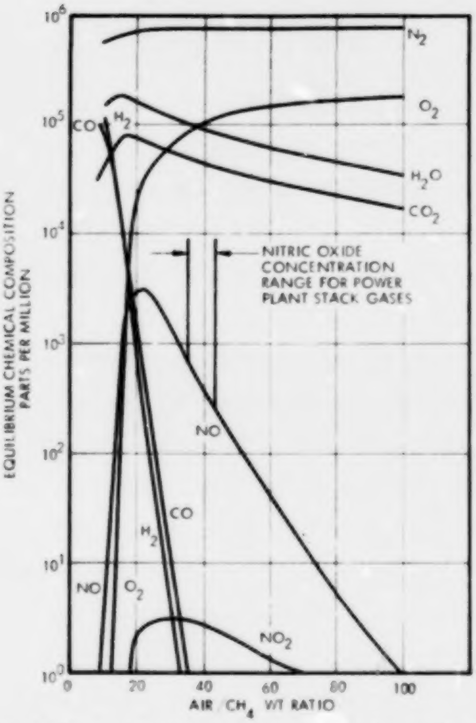

Figure 1. Equilibrium Chemical Composition of CH_4-Air Flames as a Function of Mixture Ratio

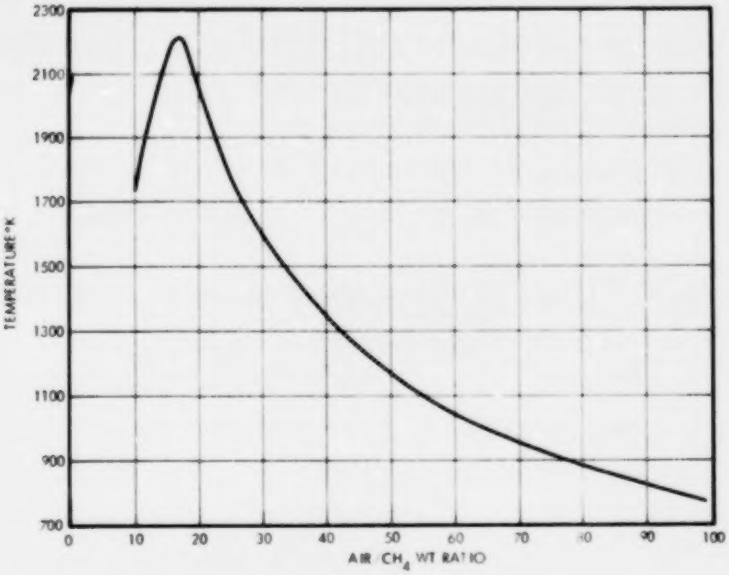

Figure 2. Adiabatic Flame Temperature as a Function of Oxidizer-Fuel Mixture Ratio for Methane-Air Flames

equilibrium concentration of nitric oxide decreases rapidly as the adiabatic flame temperature decreases. Correspondingly, the equilibrium (but not necessarily the actual) concentrations of nitric oxide will decrease as the combustion gases from a fixed source are cooled.

- Over the entire mixture ratio range, the equilibrium concentrations of nitrogen dioxide (NO_2 or N_2O_4) which can form in the flame are negligible compared with the equilibrium nitric oxide concentration. That is not to say, however, that nitric oxide which is formed in the high temperature flame will not oxidize to nitrogen dioxide either in the exhaust vent or the atmosphere.

In general, NO_x production in the high temperature combustion zone is somewhat lower than that predicted from thermochemical calculations (kinetic limitation due to short residence times). By the same token slow kinetics are responsible for the observed lack of NO decomposition or oxidation during cooling of the flue gases. Thus, the nitrogen oxide constituents of power plant flue gases at the point of atmospheric discharge equal those generated in the high temperature zone and they are the same composition (virtually all nitric oxide); the typical composition of nitrogen oxides in power plant stack gas is 90-95% NO and 5 to 10% NO_2. Flue gas NO_x abatement approaches must, therefore, be capable of controlling NO.

In addition to the formation of NO_x in flame environments by the fixation of nitrogen ($N_2 + O_2 \rightarrow 2NO$), organic nitrogen compounds present in coal and fuel oils can be oxidized to nitric oxide at temperatures well below those required for the direct formation of NO from oxygen and nitrogen.[1,2,3] This source of oxides of nitrogen is particularly important in low temperature combustion processes involving coal or fuel oil (such as fluidized bed combustion of coal) but becomes of lesser importance (with respect to nitrogen fixation) as the flame temperature of the combustion process increases.

Nitrogen oxide volume concentrations in power plant flue gases range from 0.02 to 0.15% depending on fired fuel and mode of combustion.

Technical approaches to the problem of preventing NO_x emissions from stationary combustion sources can generally be divided into two major categories:

1. Approaches which prevent the formation of NO_x in the flame environment (combustion modifications).

2. Approaches which chemically or physically remove oxides of nitrogen from the cooled combustion gases prior to venting to the atmosphere.

The first category of approaches have generally involved three types of modifications to the combustion system:

- Increasing the fuel-to-air ratio which lowers both the thermodynamic and kinetic potential for NO_x formation.

- Lowering the peak flame temperature by recirculating flue gases, staged combustion, or injecting steam or water into the combustion zone. This type of approach also lowers both the thermodynamic and kinetic potential for NO_x formation.

- Modifying the shape and size of the combustion zone to minimize the residence time of reactants in the peak temperature zones. This approach lowers the kinetic potential for NO_x formation.

Combustion modification approaches to NO_x control in stationary power stations are most attractive from an economic point of view. In principle they have the potential of being the lowest cost approach to NO_x control. However, their applicability is limited in that they are not capable in preventing all NO_x formation in the combustion zone and they can not influence NO_x formation from the oxidation of fuel nitrogen. In addition, these approaches appear difficult to apply to coal-fired boilers. For natural gas and low nitrogen oil-fired boilers, combustion modification looks attractive, especially if complete NO_x removal is not required.

In the second category of technical approaches (chemical or physical removal of oxides of nitrogen) are included:

- Direct catalytic decomposition of nitric oxide ($NO \xrightarrow{Cat.} 1/2\ N_2 + 1/2\ O_2$)
- Selective catalytic reduction of nitric oxide in the presence of excess oxidants. Proposed selective reductant systems are:

  Ammonia ($6NO + 4NH_3 \xrightarrow{Cat.} 5N_2 + 6H_2O$)

  Methane ($4NO + CH_3 \xrightarrow{Cat.} 2N_2 + CO_2 + 2H_2O$)

  Carbon Monoxide ($2NO + 2CO \xrightarrow{Cat.} N_2 + 2CO_2$)

  Hydrogen ($2NO + 2H_2 \xrightarrow{Cat.} N_2 + 2H_2O$)

  Hydrogen Sulfide ($2NO + 2H_2S \xrightarrow{Cat.} 2S + N_2 + 2H_2O$)

  The oxygen in the flue gas should not be affected by nor should it affect the catalyst.
- Nonselective catalytic reduction of nitric oxide in the presence of excess oxidants (e.g., $NO + CO + \text{excess } O_2 \xrightarrow{Cat.} CO_2 + N_2$).
- Catalytic oxidation of NO to NO_2 followed by liquid scrubbing.

- Absorption (scrubbing)

- Adsorption

Nitric oxide formed in the high temperature flame zone of a combustion process becomes thermodynamically more and more unstable as the combustion gases cool (Table 1) (however, the kinetic stability of NO increases as the temperature of the combustion gases decreases). Thus, in principle, in the presence of the proper catalyst, it should be possible to effect the low temperature decomposition of the nitric oxide present in the stack gases. This is a very appealing approach since all that would be required is to pass the combustion gases through a bed of catalysts prior to entering the stack and the nitric oxide would decompose to nitrogen and oxygen.

Table 1. EQUILIBRIUM CONCENTRATION OF NITRIC OXIDE WHICH CAN FORM FROM A STARTING MIXTURE OF 80 VOL. % N_2, 10 VOL. % O_2, AND 10 VOL. % He AS A FUNCTION OF TEMPERATURE

Temperature °K	Pressure atm	Equilibrium Concentration of Nitric Oxide, ppm
1500	1.0	919
1400	1.0	548
1300	1.0	301
1200	1.0	150
1100	1.0	66
1000	1.0	25
900	1.0	7.3
800	1.0	1.6
700	1.0	0.23
600	1.0	0.017

Next to direct catalytic decomposition of nitric oxide, the simplest catalytic approach to nitric oxide removal is selective reduction. In this approach a reductant is added to the flue gas stream in just sufficient quantities to react with the nitric oxide and a selective catalyst is chosen which will promote the nitric oxide reduction but will not promote the reduction of oxygen present in the combustion gas stream. The catalyst system must be highly selective for NO since oxygen may be present in the combustion gases in concentrations two orders of magnitude higher than the NO. In principle, this approach is very attractive since the cost of adding just enough reductant to react with the nitric oxide can be very low due to the low quantity of NO_x present.

In the nonselective NO_x reduction approach sufficient reductant (CH_4, CO, or H_2) is added to the combustion gas stream (or boiler) to completely reduce the residual oxygen and SO_2 (to sulfur) as well as the nitric oxide. The catalyst system must be active for NO (and SO_2) reduction but need not be selective.

The oxidative NO_x scrubbing approach involves catalytic oxidation of NO to NO_2 (or NO-NO_2 mixtures) followed by absorption of the oxidized products in scrubbing solutions.

As indicated in the introductory section of this report, the objective of Phase I of this program was to assess the feasibility of adapting catalytic NO_x abatement processes to power plants. Fulfillment of the objective required; (a) the thorough review of pertinent literature in order to establish the state-of-the-art on catalytic NO_x abatement, (b) the evaluation of the available data for compatibility to power plant conditions, and (c) the generation of experimental, design, and economic data where needed. The next section describes the developed data bank on catalytic NO_x abatement and summarizes the state-of-the-art on catalytic processes potentially adaptable to power plants.

REFERENCES FOR SECTION 2

1. Bartok, W. et al. Systems Study of Nitrogen Oxide Control Methods for Stationary Sources. Esso Research and Engineering Company. Final Report, Vol. 2. Publication Number GR-2-M, PS-69. November 20, 1969. (0178N)*

2. Shaw, J. T., and A. C. Thomas. Oxides of Nitrogen in Relation to the Combustion of Coal. Paper presented at Conference on Coal Science. Praque. 10 June 1968.

3. Smith, W. S. Atmospheric Emissions from Fuel Oil Combustion. Public Health Service Publication No. 999-AP-2. 1962.

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*Document Retrieval System Accession Number.

3. DEVELOPMENT OF A DATA BANK ON NO_x CATALYSTS AND CATALYTIC PROCESSES (TASK 1)

Technical and economic assessment of the use of catalysts for NO_x abatement in stationary power plants requires the assembly of a data bank containing state-of-the-art information. The data bank, stored at TRW, consists of literature pertinent to the subject which was derived from: (a) a literature survey, (b) a review of current research grants and contracts including private communications with principal investigators, (c) a review of TRW/UCLA in-house data on NO_x catalysis, and (d) interviews with representatives of catalysts and catalyst support manufacturing firms. Information on recent NO_x abatement efforts in Japan was obtained from a group of scientists and utility executives who recently visited the USA to exchange views on NO_x abatement technology and from the review article by Ando.[1]

The assembly of references from the open literature was concentrated primarily on the period 1969-1974. For the years prior to 1969 the bibliographies on catalytic NO_x abatement in systems studies and review articles by Bartok et al.[2] and Shelef and Kummer[3] (1969) and by NAPCA[4] (1970) served as the primary reference sources. A computerized search of the literature pertaining to NO_x abatement and related subjects for the period 1920-1970 revealed that the combination of the three cited bibliographies contain an essentially complete listing.

Hand searches of the literature were performed for the period 1969-mid 1973 concentrating primarily on Chemical Abstracts, Air Pollution, Air Pollution Index, Engineering Index, and Pollution Abstracts. In addition, computerized searches were made of Chemical Abstracts ("CA-Abstracts"), Engineering Index ("Compendex"), APTIC files, and IFI Plenum patent files. Listings on on-going NO_x R&D was partially derived from the Smithsonian Abstracts.

The documents (articles, patents, reviews, etc.) selected as pertinent to the program were procured for review, classified and stored in the data bank file. Unpublished data from TRW/UCLA research and from private communications with other groups engaged in NO_x abatement R&D were also included in the data bank.

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Upon receipt, the documents were keyworded, assigned accession numbers, and entered into TRW's computerized document retrieval system. The system enables document retrieval from the central file by author, keyword, or accession number. In excess of 250 documents have been entered into this retrieval system. A complete listing of them by the above three categories comprises Volume II of this report.

The documents selected for inclusion in the data bank contained information from the following areas of NO_x and NO_x-SO_x R&D:

- Decomposition and oxidation of NO_x.
- Selective and nonselective catalytic NO_x reduction with actual or synthetic flue gases and ICE (internal combustion engine) exhaust.
- Basic studies on catalytic NO_x decomposition, oxidation, and reduction.
- Basic studies on ammonia decomposition and oxidation.
- Preparation procedures for NO_x abatement catalysts.
- Simultaneous NO_x-SO_x abatement
- Economic and engineering analyses on NO_x-SO_x control processes proposed for power-plant or related source utilization.

The selected documents were classified and keyworded to reflect both broad and narrow categories for easy accession to very general and very specific information. For example, an article describing NO_x abatement by catalytic reduction on CuO catalysts was keyworded under "Stationary Source Control" and under "Copper Based Catalysts". The 28 keywords used in document classification are listed in Table 2 below.

The information retrieved through the described procedure was thoroughly reviewed in order to assess the state-of-the-art on catalytic NO_x control and to identify and assess catalysts and catalytic processes potentially adaptable to power plants. The ensuing paragraphs in this section summarize pertinent data in NO_x decomposition, selective and nonselective reduction, and oxidation. The cited bibliography is listed at the end of the chapter in the order of appearance; data bank accession numbers are also given. More detailed information in these fields can be found in the articles listed in the data bank bibliography, Volume II of this report.

Table 2. KEYWORDS USED IN CATALYTIC NO_x DOCUMENT CONTROL SYSTEM

Keyword	Refers To
1. BASE-METAL-CAT	All non-noble metal catalysts
2. CATALYT-DECOMP	Catalytic decomposition of NO_x
3. CATALYT-OXID	Catalytic oxidation of NO_x
4. CATALYT-REDXN	Catalytic reduction of NO_x
5. CU-BASED-CATAL	Copper-based catalysts
6. FLUE-GAS-CONTR	Data or information given for actual flue gases
7. MOBILE-SOURCE	Automotive NO_x control
8. NOBLE-METAL-CAT	Noble metal catalyst
9. OTHER-NOX-CAT	Catalyst other than noble, transition, and heavy metals and rare earths (e.g., Alkaline earths)
10. OXID-W/OTHER	Oxidation with oxidant other than oxygen
11. OXID-W/O_2	Oxidation with oxygen
12. PATENTS	Patented catalysts or systems
13. POWER-PLANTS	References specific for power plants
14. RARE-EARTH-CAT	Catalysts containing rare earths
15. RED-W/GAS-MIXT	Data on information given for synthetic gas mixtures
16. RED-W/SULF-COMP	Reduction with sulfur compounds
17. REDXN-W/CO	Reduction with carbon monoxide
18. REDXN-W/FUEL	Reduction with liquid hydrocarbons
19. REDXN-W/HC	Reduction with gaseous hydrocarbons
20. REDXN-W/H2	Reduction with hydrogen
21. REDXN-W/NH3	Reduction with ammonia
22. REDXN-W/OTHER	Any NO_x catalytic reduction not covered above
23. REVIEW-ARTICLES	Articles presenting a view of the field of NO_x catalysis or containing extensive bibliographies
24 SELECTIVE-CATAL	Selective reduction in the presence of O_2
25. SIM-NOX-SOX-CON	Simultaneous control of NO_x and SO_x
26. STATION-SOURCE	Stationary source control
27. TRANS-METAL-CAT	Transition metal catalysts
28. REL-MATL	Additional data related to NO_x processes

3.1 CATALYTIC NO_x DECOMPOSITION

Nitric oxide abatement from power plant flue gas by decomposition into elemental nitrogen and oxygen ($NO \rightarrow 1/2\ N_2 + 1/2\ O_2$) is theoretically the simplest, possibly the least expensive, and therefore the most desirable approach. The obvious advantage of this approach is that flue gas additives are not required. The predominant nitrogen oxide in power plant flue gas is NO which is thermodynamically unstable at stack gas temperatures. Unfortunately, its homogeneous decomposition rate is immeasurably low. Thus, the emphasis on NO decomposition has centered on catalytic approaches.

The attractiveness of this approach has lured a number of investigators into the study of NO decomposition and their conclusions have been both pessimistic and optimistic. The disagreement among investigators concerning the feasibility of this NO_x abatement approach for application to stack and exhaust gases may be largely due to the variety of conditions under which the individual studies were performed, rendering comparisons difficult, and to the requirement for severe data extrapolation before conclusions on approach applicability could be drawn. In fact, data generated with actual or simulated stack gases are virtually non-existant; there is some data generated with auto exhaust on a limited number of catalysts but at too high temperatures and space velocities to be directly relatable to power generating plants. This lack of data led to the decision to screen under this program a number of catalysts for NO decomposition potential; simulated power plant flue gas was used in these tests.

The data available in the literature as well as that generated under Task 2 suggests to us that the NO decomposition approach should not be disregarded as a potential NO_x abatement process for power plants, especially if partial NO_x removal (50 to 60%) could be considered adequate.

The ensuing paragraphs summarize the results of a number of important investigations on NO_x decomposition; complete list of citations on this subject appear in the data bank printout.

- Howard and Daniels[5] report that NO-catalyst mixtures kept sealed in tubes at ambient temperature over a half century revealed no NO decomposition.

- A large number of catalysts (commercial and laboratory prepared) were screened for NO decomposition potential by Reisz et al.[6] at IITRI (Illinois Institute of Technology Research Institute). The tests were conducted with 2000 ppm NO in nitrogen, at 500-700°C (932 to 1292°F), and at actual space velocities exceeding 100,000 hr^{-1} (>30,000 hr^{-1} STP) with only one exception (V_2O_5). Their data, as tabulated by Bartok et al.,[2] are presented in Tables 3 and 4. The data in these tables indicate that at high space velocities only the platinum on asbestos catalyst exhibited a slight NO decomposition activity (10%). The only catalyst (7% vanadia on alumina) tested at low space velocity (800 hr^{-1} STP) promoted NO decomposition to 20% at 500°C (932°F); however, the low conversion and low space velocity cast doubt on the potential of this catalyst.

- Bartok et al[2] present additional NO decomposition data generated at Southern California Edison's El Segundo Power Station by Haagen-Smit and at Battelle Memorial Institute in Columbus, Ohio by Walling; the data were obtained through private communication. According to the report, Haagen-Smith investigated over 20 materials for NO decomposition activity with particulate-free, actual power plant flue gas in the temperature range of 66 to 760°C (150-1400°F) and at space velocities in the range of 500-3500 hr^{-1}. The list included a number of support materials (alumina, silica, molecular sieves and steel wool) as well as copper, chromium, vanadium, iron, and platinum in

Table 3. RESULTS OF IIRI's STUDY OF NITRIC OXIDE DECOMPOSITION CATALYSTS - COMMERICAL CATALYSTS [2]

Catalyst	Catalyst Manufacturer	Decomposition Temperature					
		500°C (932°F)		600°C (1112°F)		700°C (1292°F)	
		SV[a]	Decomp.	SV	Decomp.	SV	Decomp.
Magnesia-alumina spinel (27-70%)	Norton, LMA-520	1880	3	2075	4		
Silica-alumina (88-12%)	Universal Oil Products	1490	4				
Silica-phosphoric acid (70-30%)	Universal Oil Products, No. 2	1940	0	2025	0		
Vanadia-silica potassium sulfate (10-65-23%)	Davison Chemical, 903	1825	0	1785	0	1785	0
Vanadia-alumina (7-93%)	Harshaw Chemical, V-X-L-523	38	20				
Hopcalite	Mine Safety Appliances	1450 135	0 0				
Chromia-alumina (19-81%)	Harshaw Chemical CR-0205	1955	0	2140	0	2100	0
Ferric oxide	Girdler G3, carbon monoxide shift	1930[b]	2				
Magnetite	Tennessee Valley Authority, ammonia synthesis	2000	0				
Nickel oxide ($NiO-SiO_2$)	University Oil Products, hydrogeneration	1820	7	1935	3		
Cobalt-molybdate ($Co-MoO_3-Al_2O_3$)	Harshaw Chemical, Co-Mo-0401 desulfurization	1840 930	0 0				
Copper oxide-alumina (10-90%)	Harshaw Chemical, Cu-0801	1255	3	1670	0		
Zinc oxide (99%)	Harshaw Chemical, Zn-0401	1870	0	1870	5		
Mossy zinc	Baker	2140	4	2045	2		
Molybdena-alumina (10-90%)	Harshaw Chemical, Mo-1202	1795	7				
Palladium-alumina (0.5-99.5%)	Baker	1900	1	1550	3	1910	1
Silver oxide-alumina (20-80%)	Harshaw Chemical, Ag-0301	1635	0	1620	0	1430	0
Tungstic oxide-alumina (10-90%)	Harshaw Chemical, W-0101	1680	0				
Platinum-asbestos (5-95%)	Baker	2000	18	2000	10	2140	7
Platinum-alumina (0.5-99.5%)	Baker	1770	5	2080	0	2085	0
Platinum-alumina (0.6-99.4%)	Baker, dehydrogeneration	2140	0	1770	0	1890	0

[a] Volumes of gas per minute per volume of catalyst.

[b] 250°C (482°F).

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Table 4. RESULTS OF IIRI's STUDY OF NITRIC OXIDE DECOMPOSITION CATALYSTS - LABORATORY-PREPARED CATALYSTS[2]

			Decomposition Temperature					
			500°C (932°F)		600°C (1112°F)		700°C (1292°F)	
	Oxide Wt. %	Alumina[c] Wt. %	SV	% NO Decomp.	SV	% NO Decomp.	SV	% NO Decomp.
Sodium oxide-alumina	10	90	1835	1	1970	0	1835	1
Potassium oxide-alumina	5	95	1840	3	1815	0	1820	0
Potassium oxide-alumina	15	85	2250	2	2090	1	2045	1
Chromium oxide-alumina	10	90	1835	0	1870	0	2060	0
Manganese oxide-alumina	10	90	2045	0	1685	0	2130	0
Iron oxide-alumina	10	90	1690	0	2000	0	2090	0
Cobalt oxide-alumina	10	90	1860	0	1860	0	1955	0
Zinc oxide-alumina	10	90[d]	1955	1	2090	1	2140	1
Strontium oxide-alumina	10	90	1910	0	1585	0	1585	0
Silver oxide-alumina	10	90	1665	0	1815	0		
Cadmium oxide-alumina	10	90	1740	0	2205	0	2220	0
Barium oxide-alumina	2.5	97.5	2140	0	1845	0	1955	0
Lead oxide-alumina	5	95	1940	0	1845	4	1860	5

[a] Volumes of gas per minute per volume of catalyst.

[b] 250°C (482°F)

[c] Harshaw Chemical, Al-0401

[d] Alcoa, XH-151

various forms. "Of the materials tested only copper oxide showed promise as a decomposition catalyst, providing a little more than 10% decomposition at test conditions". Walling tested a number of commercial catalysts, including platinum, with synthetic flue gas containing 500 ppm NO and 3% oxygen at about 3400 hr^{-1} space velocity and in the temperature range of 149-427°C (300-800°F). He observed some activity with Ni, Co, and Pt catalysts at 316°C (600°F) which diminished with exposure time; the initial activity was attributed to sorption.

- Sakaida et al,[7] working with approximately 4000 ppm NO in N_2 and using commercial 0.1% Pt-3% Ni catalyst (Al_2O_3 carrier) found conversion levels of NO as high as 30% at atmospheric pressure and at least 60% at 15 atm during decomposition at 538°C (1000°F). Space velocity was about 300 hr^{-1}, which is low for stack gas use particularly with a platinum catalyst.

- Sourirajan and Blumenthal[8] studied cobalt and copper oxide catalysts for decomposition of 300 to 2100 ppm NO over the temperature range 300-1000°C (572-1832°F). Copper oxide on silica gel was found to be the most active catalyst. AT 510°C (950°F) approximately 69% decomposition was observed.

- Shelef et al[9] were not able to duplicate the conversions reported by Sourirajan and Blumenthal; however, Shelef used a much more concentrated NO gas mixture and data comparison may not be valid. In addition, Shelef's comment that the Sourirajan data may not have been taken at steady-state conditions does not appear warranted in view of the over 300 hour activity constancy reported by the Sourirajan-Blumenthal team.

- Table 5 summarizes test conditions and NO conversions on catalysts suggested in the above citations as having NO decomposition activity. In fact, this table summarizes all the "promising" NO decomposition data generated with low NO concentration mixtures which was uncovered during the literature search performed for this program. There are several claims in the literature, especially patent literature, of catalytic systems active in NO decomposition, but insufficient or no data are presented to support the claims. For example, Stephens[10] claims that when a "small amount" of NO was injected into a helium carrier gas and passed over a praseodymia zinc oxide catalyst nitric oxide was decomposed to nitrogen and oxygen. However, actual test data was not furnished in the patent.

- Table 6 presents the NO decomposition data generated under Task 2 of this program.* The data was generated with simulated power plant flue gas (14% CO_2, 3% O_2, 5% H_2O, 1000 ppm NO, and balance N_2) but without SO_2. The SO_2 effect was to be investigated only on proven active decomposition catalysts. Under the conditions of these screening tests (400°C, 20,000 hr^{-1} STP space velocity) only platinum containing catalysts revealed NO decomposition activity meriting further investigation. One of the lead-doped copper oxides indicated 13% NO deposition, all others were below 10%. The two batches of Pt on alumina (NA-1 and NA-2) showed different activity even though according to the manufacturer they were of the same composition; this discrepancy has not been explained. The data derived from the Pt-Mo catalysts

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* In a few cases the O_2 present in the simulated flue gas led to oxidation of NO to NO_2; these data are also presented in the table. The decomposition of NO in such tests was calculated on the basis of the remaining unoxidized NO.

Table 5. DECOMPOSITION OF NO AT LOW CONCENTRATIONS

Authors	Catalyst	Space Velocity (Hr^{-1}) STP	Temperature (°C)	Decomposition of NO (%)	NO Concentration (ppm)	Reference
Reisz et al.	7% V_2O_5 on Al_2O_3	800	500	20	2000	6
	5% Pt on asbestos	42,000	500	18	2000	
	0.5% Pt on Al_2O_3	37,200	600	10	2000	
		37,100	500	5	2000	
Sakaida et al.	0.1% Pt, 3% Ni on Al_2O_3 (Girdler G-43)	1,200	538	12	~4000	7
		600	538	20	~4000	
		600	427	6	~4000	
		300	538	30	~4000	
Sourirajan and Blumenthal	CuO·SiO_2 (30%/70%)	340	510	72	1290	8
		340	380	80	892	
		1,320	510	69	892	

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Table 6. SUMMARY OF TASK 2 CATALYTIC NO DECOMPOSITION AND OXIDATION DATA

Catalyst[a]	NO Oxidation[b] (%)	NO Decomposition (%)
NA-1. (0.5% Pt on Al_2O_3, Engelhard)	0	45.2
	0	14.0[c]
NA-2. (0.5% Pt on Al_2O_3, Engelhard)	0	27.5
NA-3. (22.2% Mo, 0.1% Pt on Al_2O_3, 1/16 in spheres)	0	22.8
NA-4. (22.2% Mo, 0.1% Pt on Al_2O_2, pressed)	0	24.8
NA-5. (27% Mo on Al_2O_3, pressed)	0	2.8
NA-6. (14.7% Mo on Al_2O_3, calcined in air)	0	0.7
NA-7. (14.7% Mo on Al_2O_3, reduced 20 hrs at 480°C in H_2)	0	1.7
NA-8. (14.7% Mo on Al_2O_3, reduced 4 hrs at 700°C in H_2)		
NA-11. (15% rare earth cobalt oxide on Al_2O_3, pressed)	0	5.6
NA-12. (NA-10 + 10% Pb, Pb impregnated)	0	8.4
NA-13. (15% $Gd_2(MoO_4)_3$ on Al_2O_3, pressed)	0	0.4
NA-14. (15% Gd MoO_3 on Al_2O_3, pressed	0	0.7
NA-15. (15% $GdVO_3$ on Al_2O_3, pressed)	6.7	5.9
NA-17. (16.5% $CuO \cdot Al_2O_3$)	0	1.6
NA-21. (13.1% W on Al_2O_3, 20-30 mesh)	0	11.9
NA-22. (13.1% W on Al_2O_3, pressed)	0	13.0
NA-23. (10% WO_3 on Al_2O_3, Harshaw)	0	0.5
NA-24. (10% V_2O_5 on Al_2O_3, Filtrol)	0	6.1
NA-28. (10% mixture of 83% Fe_2O_3, 17% Cr_2O_3 on Al_2O_3	0	8.9
NA-29. (same formulation as NA-28)	0	7.3
NA-30. (same formulation as NA-28, pressed)	0	7.6
NA-35. (Fe on graphite chips)[d]	0	0
NA-36 (Fe on graphite chips)[e]	0	2.5

[a] Catalyst impregnated on 1/8 x 1/8 inch Al_2O_3 pellets unless specified. Catalyst calcined in air and not prereduced unless specified.

[b] Feed contained 1000 ppm NO, 14% CO_2, 5% H_2O, 3% O_2 (unless specified). Reaction temperature was 400°C (752°F) and space velocity was 20,000 hr^{-1} (STP).

[c] 0.5% O_2 present in this test.

[d] Impregnated from organic solution of $Fe(NO_3)_3$.

[e] Impregnated from aqueous solution of $Fe(NO_3)_3$.

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(NA-3 and NA-4) suggests that the NO decomposition value generated from catalyst NA-2 may be more representative of low Pt content catalysts. Table 6 also shows that lowering the oxygen content of the flue gas from 3% to 0.5% lowers the NO decomposition efficiency of the catalyst.

- The effect of oxygen on NO decomposition has been a somewhat controversial subject among investigators engaged in this area of work. The opinions range from negative effect to no effect to positive effect. Most reported work considers O_2 as nitric oxide decomposition inhibitor; the retarding effect has been assigned to either adsorbed molecular oxygen[11,12,13] or adsorbed atomic oxygen.[14] However, both Vetter[15] and Wise and Frech[16,17] found that oxygen had an enhancing effect on the decomposition of NO in a thermal flow reactor. The former considered that a chain reaction occurred involving oxygen atoms reacting with NO in an initiation step; the latter found that below 1000°K the decomposition of NO was heterogeneous and unimolecular. Lawson[18] found that NO will decompose catalytically in dry air but not in moist air, suggesting that the presence of water vapor and not excess O_2 is a limiting factor. In a recent study specifically designed to investigate the effect of O_2 on the decomposition of NO, Amirnazi et al.[19] observed an inhibiting effect by O_2 using 1.5 to 15% NO and from 0 to 5% O_2 on several catalysts including supported platinum; they considered the equilibrium chemisorption of oxygen on sites required for the rate-determining process of NO chemisorption as the inhibiting step. Our data indicated that oxygen enhances NO decomposition under the conditions of the Task 2 screening experiments (NA-1, 3 and 0.5% O_2 tests). The test conditions may be the responsible parameter in this controversy.

- Differences of opinion have also surfaced on the assignment of reaction orders with respect to NO. Table 7 illustrates these differences if one assumes the data from the individual tests can be compared. The investigations represented in Table 7 were performed with pure NO or with high NO concentration gas mixtures; rate data derived from them can not be safely extrapolated to power plant flue gas NO concentrations. The only exception is the work by Sakaida et al.[7] presented earlier (Table 5).

On the basis of the data presented, the platinum catalyst was selected as the only one meriting further investigation. Thus, platinum was scanned under Task 2 for temperature and space velocity effects on its activity toward NO decomposition. The data derived from batch NA-2 is shown in Figure 3. Both temperature and space velocity influenced the extent of NO decomposition. A maximum was obtained during the temperature effect tests which appears to indicate that further variation of this parameter will not improve decomposition; lower space velocities, however, may increase NO conversion further provided economics permit them. The 52.5% NO decomposition at 300°C and 10,000 hr^{-1} (STP) S.V., if proven valid in long-term tests,* may be adequate for certain applications even if not improvable. The effect of SO_2 was not investigated during these tests, but if extrapolations from the SO_2 effect on the ammonia -NO_x-Pt system are valid, SO_2 should not affect this catalyst at decomposition temperatures exceeding 300°C (572°F).

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* These data were taken at steady-state conditions at an approximate rate of one point per hour; all data was reproduced. These tests were run long enough to preclude the possibility that NO decomposition was really NO sorption.

Table 7. DECOMPOSITION OF NITRIC OXIDE ON VARIOUS CATALYSTS. REACTION ORDER WITH RESPECT TO NO

Authors	Catalyst	Reactor	Gas Mixture	Temperature range, °C	Pressure Torr	Reaction order with respect to NO	Reference
Fraser and Daniels	Metal oxides	Flow	10% NO in He	740-1040	760	0	14
Yur'eva et al.	Transition metal oxides	Recycle	100% NO	250-750	100-380	2	20
Shelef et al.	Supported Pt and oxides	Flow	4-100% NO in He	279-938	760	$\sim$1[a]	21
Winter	Oxides	Recycle	100% NO	330-870	50-400	1	22
Backman and Taylor	Pt wire	Batch	100% NO	1210	201-479	2	12
Zawadski and Perlinsky	Pt-Rh wire	Batch	100% NO	860-1060	100	1	23
Green and Hinshelwood	Pt wire	Batch	100% NO	882-1450	200-500	1	11
Sakaida et al.	Supported Pt-Ni	Flow	0.404 and 0.432% NO in N_2	427-538	1-15 atm	2	7
Amirnazmi et al.	Oxides	Flow	1.5-15% NO 0-5% O_2 in He	450-1000	780-960	1	19
Amirnazmi et al.	Supported Pt	Flow	1.5-15% NO 0-5% O_2 in He	450-1000	780-960	1	19
Harding	Al_2O_3	Flow	10-15% NO in He	644-807	760	2	24

[a] A commercial Pt catalyst also tested in this study resulted in NO order of 0.5.

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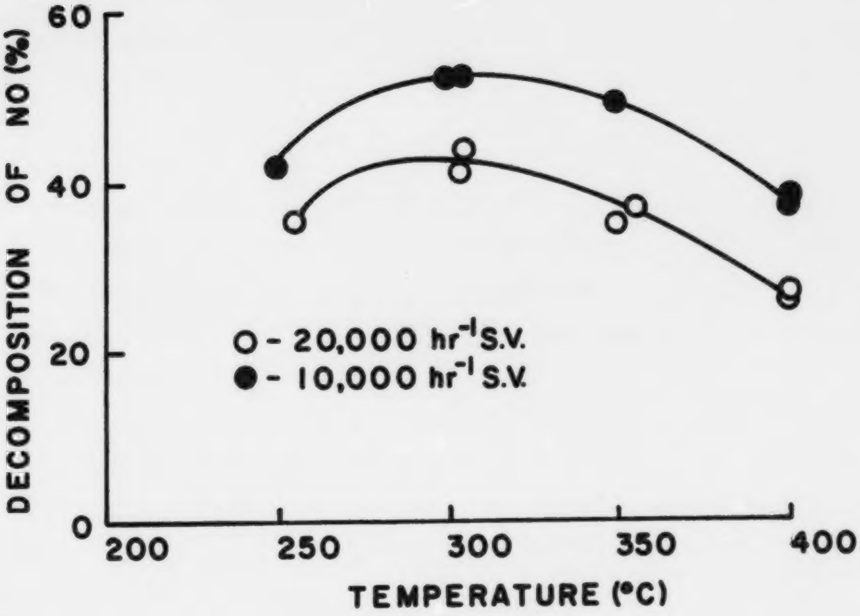

Figure 3. Decomposition of NO on Pt Catalysts

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3.2 SELECTIVE CATALYTIC REDUCTION OF NO_x

Selective catalytic reduction of NO_x rates second only to decomposition in desirability as an NO_x abatement process. Since NO_x in power plant flue gas coexists with from one to two orders of magnitude larger quantities of oxygen it is highly desirable to selectively reduce NO_x without affecting or being affected by the oxygen present. A number of investigators have been pursuing this avenue of NO_x abatement and the results appear promising with some systems (e.g., NH_3).

The principal reductants proposed for NO_x selective reduction are carbon monoxide, hydrogen, and ammonia. Others include sulfides, various amines hydrazine and urea. Experimental data in the latter group is virtually nonexistant and none was generated in Task 2. The reasons for treating these latter reductants as unattractive range from cost (hydrazine, urea) to toxicity (H_2S). In the subsections that follow representative investigations on selective NO_x reduction by CO, H_2 and NH_3 on noble and non-noble metal catalysts are presented; a more complete citing of selective catalytic NO_x reduction investigations can be found in the data bank printout.

3.2.1 Selective NO_x Reduction by Carbon Monoxide and Hydrogen

A review of the pertinent literature as well as the data generated under Task 2 failed to identify a promising catalyst for the selective reduction of NO_x by either CO or H_2, especially one that could be used for power plant NO_x abatement. Under special conditions (low space velocity, low O_2 to NO ratio, dry flue gas) iron oxide exhibited some activity for NO reduction with CO in the presence of O_2 at approximately 150°C. Also, certain noble metal catalysts promoted the selective reduction of NO with H_2 at approximately 300°C provided sulfur and a number of metallic compounds were not present in the flue gas stream. Neither of these catalytic systems can be presently recommended as meriting further study toward utilization in power plans, but one can not rule out a future catalytic scheme involving selective NO_x reduction by CO or H_2; the search for a selective catalyst for these reactions continues.

Two approaches have been employed in the search for an active and selective NO-CO or NO-H_2 catalyst. The first involves the identification of reaction parameters or catalyst constituents that favor the NO_x reduction reaction over that of oxygen reduction; the second involves attempts to retard ("poison") the oxygen reduction process so that NO_x reduction takes over. The ensuing paragraphs outline representative investigations on selective NO_x reduction with CO and H_2 (catalytic) and summarize the data from the screening tests performed under Task 2.

- Early work in this area was performed at the Franklin Institute by Taylor[26] who showed that O_2 had a detrimental effect on the reduction of NO by CO when the CO concentration was less than that required to reduce both oxygen and NO. In fact, he showed that CO reacted preferentially with O_2 on various chromites and chromite promoted iron.

- Sourirajan and Blumenthal[8,27] confirmed the nonselectivity of CO, concluded that oxygen was not a catalyst "poison" but a competing reactant, and suggested the two-stage catalytic converter approach to auto-exhaust purification rather than continued search for selective NO-CO catalysts.

- Shelef, et al.[28] investigated several transition metal oxides for selective activity toward the NO-CO reaction in the presence of oxygen; but none of the oxides indicated selectivity. However, when the CO-NO and CO-O_2 reactions were studied separately, the NO reduction reaction exhibited a higher rate than the O_2 reduction rate on supported Fe_2O_3 and CrO_3 at low temperatures; representative data is summarized in Table 8. According to these investigators the average oxidation state of these catalysts was lower when oxygen was not present;

Table 8. RELATIVE EFFECTIVENESS OF SUPPORTED CATALYSTS FOR THE CO-NO AND $CO-O_2$ REACTIONS [28]

Supported Catalyst	Temperature (°C) of 50% CO Removal	
	CO-NO	$CO-O_2$
Fe_2O_3	145	180
$CuCr_2O_4$	155	115
Cu_2O	175	140
Cr_2O_3	220	265
NiO	250	220
Pt	285	215
Co_3O_4	350	115
Bare Support	425	365
MnO	435	195
V_2O_5	560	405

Flow rate 1400 cc/min, catalyst volume 80 cc.

Inlet gas composition in CO-NO reaction ~1.2% CO; 2% NO.

Inlet gas composition in $CO-O_2$ reaction ~1.2% CO; 1.2% O_2.

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it was, therefore, implied that the lower valence state of the catalysts favored NO reduction. In another study Shelef and Kummer[3] showed that at a very narrow temperature range (near 170°C) and very low space velocities Fe_2O_3 reduced NO to N_2O in the presence of oxygen; the data is shown in Figure 4. Even lower dips in reactor outlet NO concentration were observed by Bauerle et al.[29] with near stoichiometric oxidant-reductant gas mixtures but on noble metal catalysts (platinum, rhodium). It appears questionable whether the indicated "dips" in NO concentration represent true selectivity or merely parallel reactions at nearly equal rates. In any case, the above experiments were performed under conditions which can not be extrapolated to power plant flue gas conditions (high NO/O_2 ratios, no water vapor). It is conceivable that a catalyst exists whose "light off" temperature for the CO-NO reaction is substantially lower than that of the CO-O_2 reaction so that the desired selectivity at adequate rates would materialize; the data reviewed has not hinted such a catalyst.

- Sorensen and Nobe[30] investigated the NO-CO and O_2-CO reactions on lead doped CuO catalysts. They found that lead retarded the O_2-CO reaction while it appeared to enhance the NO-CO reaction. In the current program we tested the above reactions simultaneously on several lead doped CuO catalysts in an attempt to induce NO-CO selectivity by "poisoning" the O_2-CO reaction; under the test conditions utilized the attempt failed.

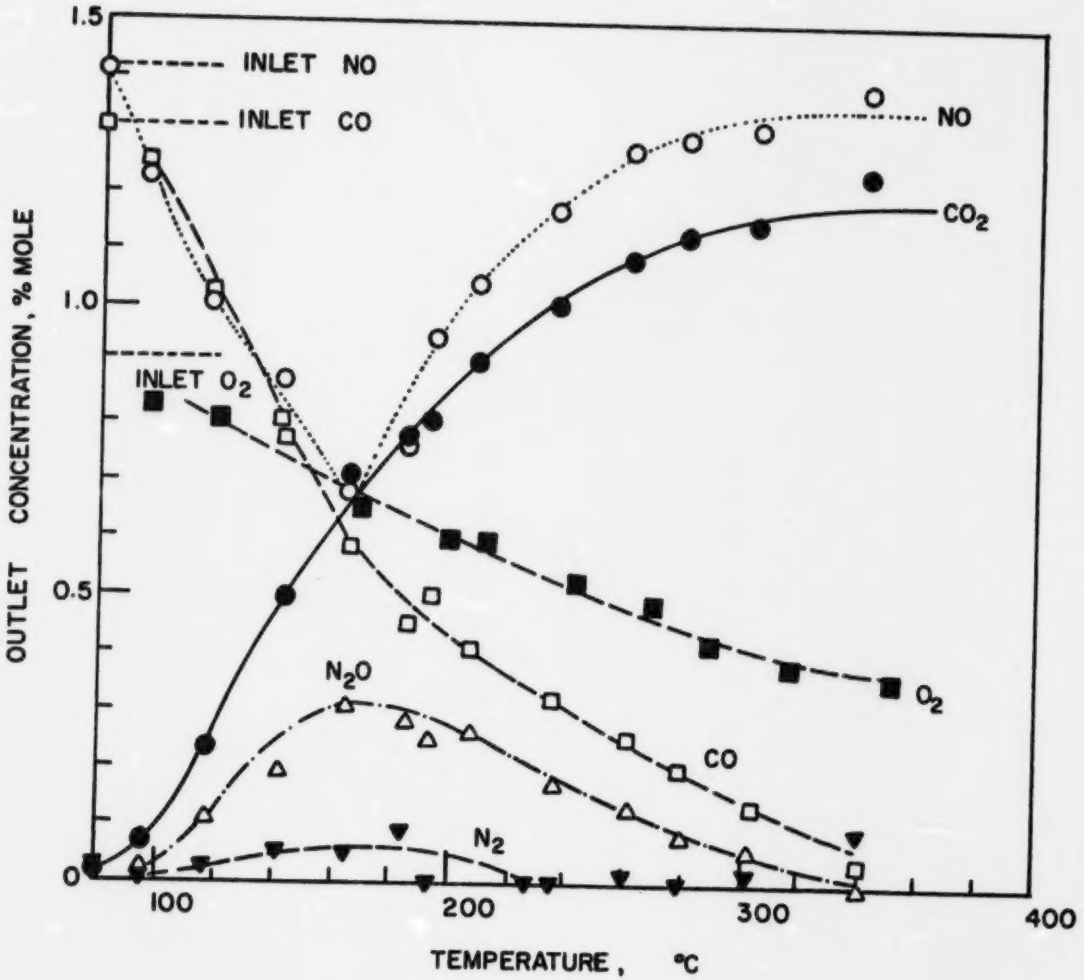

Figure 4. Reduction of NO and O_2 on Fe_2O_3 as a Function of Temperature [3]

- The data on selective catalytic NO_x reduction with H_2 is very similar to that described for CO. Partial selectivity has been reported[3] on certain Pt and Pd catalysts at low temperatures and with sulfur-free gas mixtures. Jones et al.[25] report that "under certain conditions, many supported noble metal catalysts are capable of promoting the removal of NO from automobile exhaust, even in the presence of large amounts of oxygen.... The catalysts which exhibit the selective nitric oxide reduction are very sensitive to poisoning, particularly by sulfur". The tests were performed on commercial noble metal catalysts. Table 9 summarizes some of the data which may be considered pertinent to this program. The data indicates that NO conversion strongly depends on NO inlet concentration. Conversion of NO to NH_3 was not high, but most of the NO was reduced to N_2O (not indicated in the table). Transition metal oxides did not indicate activity toward the NO-H_2 reaction in the presence of oxygen.

Table 9. REDUCTION OF NO WITH H_2 ON CATALYST PZ-1-168 (SUPPORTED Pt, UOP) IN THE PRESENCE OF OXYGEN[25]

NO Inlet Conc. (ppm)	NO Reacted, (%)	NH_3 Formed, (ppm)	Inlet NO Converted to NH_3, %	Reacted NO Converted to NH_3, ppm
3450	82.5	95	2.75	3.33
1900	83.5	69	3.63	4.35
885	77.5	28	3.16	4.08
500	64.0	19	3.80	5.94
245	32.6	13	5.30	16.30

Carrier gas: N_2; H_2 inlet conc.: 1.43%; O_2 inlet conc.: 0.9-1.0%; Space velocity: 20,000 hr^{-1}; reaction temperature: 200°C (392°F)

- Table 10 summarizes the data generated in Task 2 as a part of the catalyst screening test matrix. The tests were performed with simulated flue-gas to which 1000 ppm of CO or H_2 were added (the flue gas contained 1000 ppm NO and 3% O_2). The test temperature was 400°C and the space velocity 20,000 hr^{-1}. The data strongly resembles that obtained during the NO decomposition tests (Table 6); the implication appears to be that the observed NO conversions are not due to selective NO reduction by CO or H_2 but to NO decomposition. In view of the Jones data, which indicated that the optimum temperatures for these selective reduction reactions were in the 150 to 300°C range, the Task 2 tests were performed at higher than optimum temperature; it is conceivable that at a lower temperature some NO reduction with CO or H_2 could have taken place, but it is very improbable that the extent of reaction would have been such as to alter our negative conclusion with respect to practical application or potential of these selective processes.

There have been several additional studies on NO-CO, NO-hydrocarbon, and NO-H_2 reactions in the presence or absence of oxygen which have been included in the data bank citations (Volume II of this report). The majority of these investigations represent basic studies on the above reactions with no hint of selectivity; their discussion is beyond the scope of this report since the data can not be related to potential application for NO_x abatement from power plants.

3.2.2 Selective NO_x Reduction by Ammonia

Ammonia is generally considered to be the only relatively inexpensive, truly selective NO reductant in the presence of oxygen. In fact, many investigators of the catalytic reduction of NO by NH_3 have shown that oxygen enhances the reduction rate up to a certain temperature which depends on the catalyst used. Markvart and Pour[31] have suggested that NH_3 dissociation on the catalyst surface is the controlling step in the NH_3-NO reaction; NO

Table 10. SUMMARY OF TASK 2 DATA ON SELECTIVE REDUCTION OF NO WITH CO AND H_2

Catalyst[a]	O_2 in Feed[b] ( )	Apparent NO Reduction By CO (1000 ppm)	Apparent NO Reduction By H_2 (1000 ppm)
NA-1. (0.5% Pt on Al_2O_3, Engelhard)	3	46.0	46.6
	0.5	22.6	19.4
NA-3. (22.2% Mo, 0.1% Pt on Al_2O_3, 1/16 in spheres)	3	25.0	26.9
	0.5	14.9	12.3
NA-4. (22.2% Mo, 0.1% Pt on Al_2O_3, pressed)	3	30.8	28.1
	0.5	14.3	18.9
NA-5. (27% Mo on Al_2O_3, pressed)	3	1.3	2.6
	0.5	0.5	2.4
NA-6. (14.7% Mo on Al_2O_3)	3	2.6	1.4
	0.5	2.2	0.5
NA-7. (14.7% Mo on Al_2O_3, reduced 20 hrs at 480°C in H_2)	3	1.8	2.9
	0.5	0.8	0.6
NA-11. (15% rare earth cobalt oxide on Al_2O_3, pressed)	3	0	4.9
	0.5	0	3.7
NA-12. (NA-10 + 10% Pb)	3	13.1	8.4
	0.5	3.9	9.9
NA-13. (15% Gd_2VO_3 on Al_2O_3, pressed)	3	3.3	2.1
	0.5	6.6	2.2
NA-15. (15% $GdVO_3$ on Al_2O_3, pressed)	3	1.5	8.0
	0.5	10.4	3.9
NA-17. (16.5% $CuO \cdot Al_2O_3$)	3	0	8.0
	0.5	4	3.9
NA-18. (With 1% Pb NA-17)	3	11.0	7.8
	0.5	9.4	5.6
NA-19. (With 5% Pb NA-17)	3	0.4	3.6
	0.5	2.5	2.7
NA-20. (With 10% Pb NA-17)	3	2.3	2.7
	0.5	3.0	4.8
NA-21. (13.1% V on Al_2O_3, 20-30 mesh)	3		13.5
	0.5		22.3
NA-24. (10% V_2O_5 on Al_2O_3, Filtrol)	3	3.8	3.4
	0.5	0	1.1
NA-26. (Girdler G3A, Iron Chromium)	3	0	4.8
	0.5	1.0	3.0
NA-28. (10% mixture of 83% Fe_2O_3, 17% Cr_2O_3 on Al_2O_3)	3	3.8	4.0
	0.5	2.0	2.7
NA-29. (Same formulation as NC-28)	3	4.1	3.0
	0.5	1.4	1.7
NA-30. (Same formulation as NC-28, pressed)	3	4.4	5.7
	0.5	1.[illegible]	1.9
NA-35. (Fe on graphite chips)[c]	3	0	1.2
	0.5	0	18.0
NA-36. (Fe on graphite chips)[d]	3	1.0	0.7
	0.5	1.1	0

[a] Feed also contained 1000 ppm NO, 14% CO_2, 5% H_2O, 1000 ppm H_2 in N_2, 400°C. 20,000 hr^{-1} space velocity.

[b] Catalyst impregnated on Al_2O_3 pellets unless specified. Catalyst calcined in air and not prereduced unless specified.

[c] Impregnated from organic solution of $Fe(NO_3)_3$.

[d] Impregnated from aqueous solution of $Fe(NO_3)_3$.

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reacts with most of these fragments to form N_2 and/or N_2O. When O_2 is present, ammonia fragment consumption is higher (including fragments that do not react with NO); thus, the catalyst surface is freed faster and both the NO reduction rate and extent of reduction increase (equilibrium shift). A more sophisticated NO-NH_3 reaction mechanism is offered by Otto et al.[32,33,34] in a series of papers involving Cu, Ru, and Pt catalysts; however, the inferences concerning the rate determining step and the oxygen effect appear to be the same.

The literature survey performed in this program as well as the UCLA investigations (Task 2) strongly suggested that a catalytic process involving the selective NH_3-NO reaction is potentially adaptable to power plants for efficient NO abatement. The above sources suggested both noble and non-noble metal catalysts for this purpose. Non-noble metal catalysts are less active and therefore less efficient than noble metal catalysts, but they are also much less expensive and possibly more resistant to poisoning (especially sulfur). Promising catalysts include: Pt, vanadia, Fe-Cr oxide mixtures, Mo, Cu-Pb and La-Cu-Zr. Most of the data on the catalyst-NH_3-NO_x-O_2 process has been obtained on platinum in connection with nitric acid plant tail gases; data on non-noble metal catalysts was principally derived from patents and Task 2 investigations. The next few paragraphs present a summary of representative investigations on selective NO_x reduction by NH_3 derived from the open literature and Task 2 tests.

- Newman and Rose[35] studied the oxidation of ammonia on platinum and concluded that the production of nitrogen was the result of a secondary reaction between product nitric oxide and ammonia. They also reported that in the system Pt-NO-NH_3-O_2 the product N_2 below 500°C is derived from the NO-NH_3 reaction while at temperatures above 500°C from the O_2-NH_3 reaction. The same observation was made during later studies (including Task 2), but the temperature where the oxygen takes over appears to be lower than 500°C; there is also a temperature range (probably between 300-400°C) where both NO and O_2 contribute to N_2 production.

- The majority of work on selective NO_x reduction by ammonia on noble metals (Pt, Pd, and Ru) was performed by Andersen and co-workers,[36] who also investigated cobalt and nickel They report that Pt is by far the most efficient catalyst in the above group for selective NO_x reduction by ammonia. With an NH_3 to NO ratio of one in a gas containing 10 moles of O_2 per mole NH_3, catalytic action was sufficiently selective to reduce NO to 10 ppm from approximately 3000 ppm. A summary of the data is presented in Figures 5 and 6. The first set of data indicates that space velocity has no effect on NO_x reduction in the temperature range of 200 to 350°C and that maximum conversion occurs at 200 ± 50°C. The data in Figure 6 indicates that reactor pressure, water vapor content (up to 1.6%), and the NH_3 to NO ratio (above one) have no effect on NO reduction. Salt formation (mostly ammonium nitrate) was observed in the catalyst reactor effluent at "low temperatures"; neither the quantity nor the exact composition of these salts were reported.

  The Pt catalyst was tested for 3 months without signs of activity deterioration. However, Bartok et al.[2] state that according to information received from Andersen the noble metal catalysts are easily poisoned by sulfur and their use is restricted to gases containing less than 1 ppm sulfur compounds. NO_2 present in the catalytic reactor feed deactivated most of the Pt catalysts, also (Andersen); a specially prepared Pt catalyst (MPS 900) alleviated the latter problem. The improved Engelhard catalyst has been successfully incorporated into monolith forms; Table 11 presents data taken on nitric acid plant tail gas with this catalyst.[37]

- Environics, Inc.,[38] is currently investigating, at a pilot plant scale, the selective reduction of NO_x with NH_3 on Pt under EPA contract. The flue gas is drawn

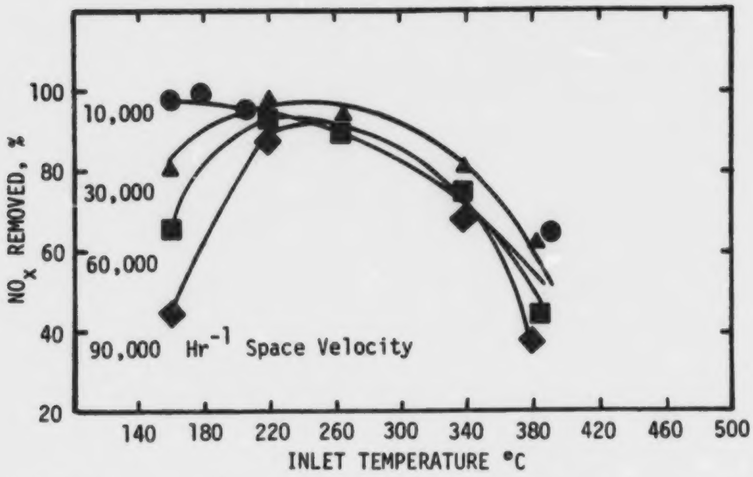

Figure 5. Selective NO_x Reduction by NH_3 on Pt as a Function of Temperature and Space Velocity [36]

(Catalyst: 0.5% Pt on Al_2O_3; Inlet gas: 3% O_2, 0.3% NO, 0.3% NH_3, 0.8% H_2O; pressure 100 psig)

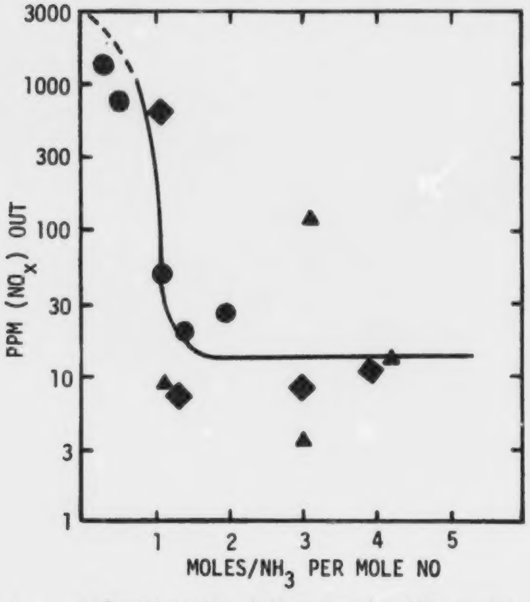

Figure 6. Selective NO_x Reduction by NH_3 on Pt as a Function of NH_3/NO and Space Velocity [36]

3.4% O_2, 0.28% NO, 0% H_2O, 149-166°C, 0 psig
3.4% O_2, 0.28% NO, 1.6% H_2O, 149-166°C, 0 psig
3.0% O_2, 0.30% NO, 0.66% H_2O, 163-180°C, 100 psig
(Catalyst: 0.5% Pt on Al_2O_3)

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Table 11. SELECTIVE TREATMENT OF NITRIC ACID PLANT TAIL GAS [37]

Catalyst: NCM-S900 (Honeycomb)
Fuel: NH_3
Operation Pressure: 100 psig

Tail Gas Composition: 0.3% NO + NO_2
3.0% O_2
0.9% H_2O
Balance N_2

Number	Percent of Fuel	Percent Fuel Over Stoichiometric[a]	Space Velocity (Hr^{-1})	Inlet Temperature (°C)	Residual N-Oxides		Effluent NH_3 (ppm)
					NO_2 (ppm)	NO + 1/2NO_2 (ppm)	
1	0.46	50	20,000	259	0	31	10
2	0.46	50	50,000	255	0	82	10
3	0.37	20	100,000	223	0	100	198
4	0.42	40	100,000	226	50	86	--
5	0.37	20	150,000	239	20	171	308
6	0.46	50	150,000	232	20	193	318

[a] Assuming equal amounts of NO and NO_2 to be present.

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from a 60 MW gas fired power plant unit. The catalyst, 0.3% Pt on a monolith, is mounted on a rotating heat exchanger unit similar to units used in air preheaters. The disc rotates between flue gas and inlet air stream. Flue gas enters the unit at approximately 300°C and exits at 255°C while the counter flow air is heated to about 150°C. The rotating catalyst bed is approximately 0.22 M^3 (8 ft^3); only half of the catalyst is in the flue gas stream at any time. At space velocities up to 50,000 hr^{-1}, inlet NO_x concentrations averaging 200 ppm, and NH_3 to NO_x ratios between 2 and 4, 90% or better NO_x conversions have been consistently achieved during six months of operation with sulfur-free flue gas. A substantial portion of the reduced NO_x appeared as N_2O (private communication information).

- Other investigations involving noble metal and non noble metal mixtures include the following: Gajewski et al.[39] successfully used a Pt on alumina catalyst for the selective reduction of NO with NH_3 at a semicommercial size HNO_3 plant (30 m^3/hr tail gas). Jones and Weaver[40] tested successfully Pt and CuO oxide catalysts on auto exhaust to which ammonia had been added for the selective reduction of NO; amines and ammonium salts are suggested as substitutes for ammonia. Griffing et al.[41] received a patent on the use of CuO-Pt and CuO catalysts for the selective reduction of NO by NH_3 in auto exhaust; they recommend 316-427°C (600-800°F) with the CuO-Pd catalyst and 371-649°C (700-1200°F) with CuO.

- A number of non-noble metal catalysts have been proposed for use in the selective reduction of NO_x with ammonia in the presence of oxygen, but data on them are limited. The available data, derived principally from patent literature, is summarized in Table 12 (This table also includes data on Pt not presented earlier). Non-noble metal catalysts suggested or claimed (patents) to be efficient promoters of the NO_x-NH_3 selective reduction reaction include the following: copper oxide, iron base NH_3 decomposition catalysts, vanadia, manganese dioxide, moly, tungsten trioxide, iron-chromium oxide mixtures, cobalt oxide, and zirconium promoted lanthanum cuprate. The majority of these catalysts have been proposed for nitric acid tail gas treatment or auto exhaust NO_x abatement, but the data suggests that they may also be candidates for power plant use. Several of the Table 12 catalysts, or catalysts of similar composition, were screened under Task 2 of this program with synthetic power plant flue gas. Alumina supported vanadia and certain mixtures of iron-chromium oxides proved to be efficient selective NO_x-NH_3 catalysts. CuO and WO_3 exhibited little or no activity. Mo, Fe, Cr, and Co based catalysts varied from low to medium activity. Catalyst composition and method of preparation appeared to have a pronounced effect on catalytic activity with certain groups, especially the Fe-Cr catalysts.

- Table 13 lists the catalysts screened under Task 2 for NH_3-NO-O_2 activity and the percent NO reduction attained with each of them. The tests were conducted with synthetic flue gas (1000 ppm NO, 3% O_2, 14% CO_2 5% H_2O, balance N_2) to which near stoichiometric quantities of NH_3 with respect to NO were

Table 12. PUBLISHED DATA ON SELECTIVE REDUCTION OF NO WITH NH_3 IN SIMULATED OR ACTUAL FLUE GAS

Author	Catalyst	NH_3/NO Inlet	Space Velocity (hr^{-1})	Temperature (°C)	NO Inlet Conc. (ppm)	Conversion of NO (%)	Remarks	Reference
Gajewski, et al.	0.2%Pt-Al_2O_3	1.5-2.0	40,000	250	3000	95	No mention of N_2O production; little NH_3 unconsumed; tested at 300,000 lb/hr in HNO_3 plant tail gas.	39
Environics, Inc.	Pt-Al_2O_3	4	45,000	250	200	90	N_2O production confirmed, actual flue gas used	38
Jones and Weaver	0.3%Pt-Al_2O_3	0.8-1.0	~50,000	312	665	56	Tested in auto exhaust (0.5-2%O_2), space velocity and NH_3/NO ratio estimated from engine data	40
Jones and Weaver	5%CuO-Al_2O_3	0.8-1.0	50,000	379	590	84		
Griffing, et al.	5% Cu-0.5% SiO_2-Al_2O_3	1.0	24,000	450	1100	55	Space velocity and NH_3/NO ratio estimated from I.C. engine operating data.	41
Atroshchenko, et al.	Fe-based NH_3 synthesis catalyst	0.93	10,000	330	1000	100	Tested in HNO_3-plant tail gas (3% O_2 present).	42
		0.93	40,000	400	1000	80		
Atroshchenko, et al.	Fe-based NH_3 synthesis catalyst	0.98	10,000	200	1350	41	3.2% O_2 present	43
		0.98	10,000	300	1350	95		
Atroshchenko, et al.	V_2O_5	0.93	10,000	310	1000	84	3% O_2 present	42
	MnO_2	0.93	10,000	220	1000	93		
Nonnenmacker and Kartte	6.8% V_2O_5 Corundum	1.0	10,000	220	4300	98	3.5%O_2	44
		1.0	10,000	177	4300	89	3.5%O_2	
	8.9% V_2O_5·SiO_2	2.0	10,000	220	4300	79	3.5%O_2	
		2.0	10,000	270	4300	91	3.5%O_2	
		2.0	5,000	210	4300	94	3.5%O_2	
	6.8% V_2O_5-αAl_2O_3	1.0	15,000	246	3800	100	4%O_2	
	6.8% V_2O_5-αAl_2O_3	2.1	20,000	382	2350	96	NO_2 present, actual NHO_3 plant tail gas.	
	10% MoO_3-Al_2O_3	2.6	3,000	398	3000	80		
	10% WO_3-Al_2O_3	1.0	10,000	288	4300	100		
Schmidt and Schulze	85% Fe_2O_3 10% Cr_2O_3 2% CrO_3	1.0	1200	300	135	100	NO_2 present, no content shown includes NO_2; space velocity calculated assuming a density of unity for the catalyst	45
	The above +3% SiO_2, Alkali metal or alkaline earths	1.0	1200	250	3000	100	2-4% O_2, No CO_2 present.	
Jaros and Krinzek	10% Co_3O_4 on Al_2O_3	2.3	10,000	185	3300	61	3% O_2 present.	46
	0.5% Pt on Al_2O_3	2.3	30,000	200	2200	96	3% O_2 present	
Kudo, et al.	Zr-promoted La CuO_3 on Al_2O_3 (Unspecified concentration)	0.8	21,000	350	700	90	1% O_2, 12% CO_2, 12% H_2O, 1000 ppm SO_2 balance N_2	47
		0.7	40,000	350	700	70		

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Table 13. SUMMARY OF TASK 2 DATA ON SELECTIVE REDUCTION OF NO WITH NH_3

Catalyst[a]	Reduction of NO[b] (%)
NA-1 (0.5% Pt on Al_2O_3)	31.8
NA-2 (0.5% Pt on Al_2O_3)	9.8
NA-3 (22.2% Mo, 0.1% Pt on Al_2O_3, 1/16-in. spheres)	38.0
NA-4 (22.2% Mo, 0.1% Pt on Al_2O_3, pressed)	46.1
NA-5 (27% Mo on Al_2O_3, pressed)	46.4
NA-6 (14.7% Mo on Al_2O_3)	39.7
NA-7 (14.7% Mo on Al_2O_3, reduced 20 hours at 480°C in H_2)	45.6
NA-8 (14.7% Mo on Al_2O_3, reduced 4 hours at 700°C in H_2)	45.2
NA-9 (2.7% Co_3O_4, 15% MoO on Al_2O_3, Filtrol)	14.6
NA-11 (Rare earth cobalt oxide, pressed)	35.3
NA-12 (NA-10 with 10% Pb)	4.7
NA-13 (15% $Gd_2(MoO_4)_3$ on Al_2O_3, pressed)	6.0
NA-14 (15% $GdMoO_3$ on Al_2O_3, pressed)	11.7
NA-15 (15% $GdVO_3$ on Al_2O_3, pressed)	61.2
NA-17 (16.5% CuO on Al_2O_3)	37.2
NA-18 (NA-17 with 1% Pb)	52.0
NA-19 (NA-17 with 5% Pb)	53.7
NA-20 (NA-17 with 10% Pb)	51.9
NA-22 (13.1% W on Al_2O_3, pressed)	16.0
NA-23 (10% WO_3 on Al_2O_3, Harshaw)	3.2
NA-24 (10% V_2O_5 on Al_2O_3, Filtrol)	60.3
NA-25 (10% V_2O_5 on Al_2O_3, Harshaw)	63.7
NA-26 (Girdler G3A, Iron-chromium)	17.4
NA-27 (Girdler G3A - 2nd sample)	2.7
NA-28 (10% mixture of 83% Fe_2O_3, 17% Cr_2O_3 on Al_2O_3)	67.1
NA-29 (Same formulation as NA-28)	61.6
NA-30 (Same formulation as NA-28, pressed)	32.2
NA-31 (15% Cr_2O_3 on Al_2O_3, pressed)	36.9
NA-32 (15% Fe_2O_3 on Al_2O_3, pressed)	45.7
NA-33 (15% Fe_2O_3 on Al_2O_3)	49.2
NA-34 (20% Fe_2O_3 on Al_2O_3, Harshaw)	15.7
NA-35 (Fe on graphite chips)[c]	12.0
NA-36 (Fe on graphite chips)[d]	5.8

[a] The catalysts were prepared by impregnation of 1/8 x 1/8 inch alumina cylinders and calcined in air unless otherwise specified.

[b] Simulated feed flue gas composition: 1000 ppm NO, 700-1200 ppm NH_3, 14% CO_2, 3% O_2, 5% H_2O in N_2; reactor temperature: 400°C, space velocity 20,000 hr^{-1}.

[c] Impregnated from organic solution of $Fe(NO_3)_3$

[d] Impregnated from aqueous solution of $Fe(NO_3)_3$.

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added; the reaction temperature was 400°C (752°F) and the space velocity 20,00 hr^{-1} (STP). The vanadia based catalysts (NA-15, 24, 25) and the UCLA prepared (impregnated) Fe-Cr oxide mixture catalysts (NA-28 and 29) promoted the highest percent NO reduction (>60%). The lead doped CuO (NA-18, 19, 20) promoted 52-54% NO reduction but unleaded CuO only 37% (NA-17). Moderate catalytic activity, 35 to 49% NO reduction, was exhibited by Mo-Pt catalysts (NA-3 and 4), supported molybdena (NA-5, 6, 7, and 8), a rare earth-cobalt oxide mixture (NA-11), supported chromia (NA-31), and supported iron oxides (NA-32and 33). Approximately one-half of the catalysts screened showed little or no activity including the commercially prepared Fe-Cr oxides and WO_3. The Pt-Al_2O_3 catalysts (NA-1 and 2) were subjected to the same screening test for reference; as expected they were not very active at 400°C. High NO reduction was obtained with platinum in the 200-250°C (392-482°F) range.

On the basis of the data presented in Tables 12 and 13 several catalysts could be labeled potential candidates for the selective NO_x-NH_3 reaction meriting additional experimental evaluation for ultimate use in power plants. Two of them, iron-chromium oxide mixture and vanadia, appeared to be the best and they were, thus, selected for a brief parametric investigation which included the following: NH_3 to NO ratio, NO concentration, space velocity, temperature, oxygen and SO_2 effects. Platinum was also subjected to the same investigation for reference. These experiments, including the screening tests, and the data derived from them are described in detail in Section 4. A brief summary of the results and conclusions from the parametric investigations is presented below.

Figure 7 depicts data taken on UCLA prepared Fe-Cr oxide catalysts at five NH_3 to NO ratios, three space velocities, three inlet NO concentrations, and two catalyst bed sizes. Substantial effects on NO conversion were observed with the NH_3 to NO ratio and with space velocity; the other

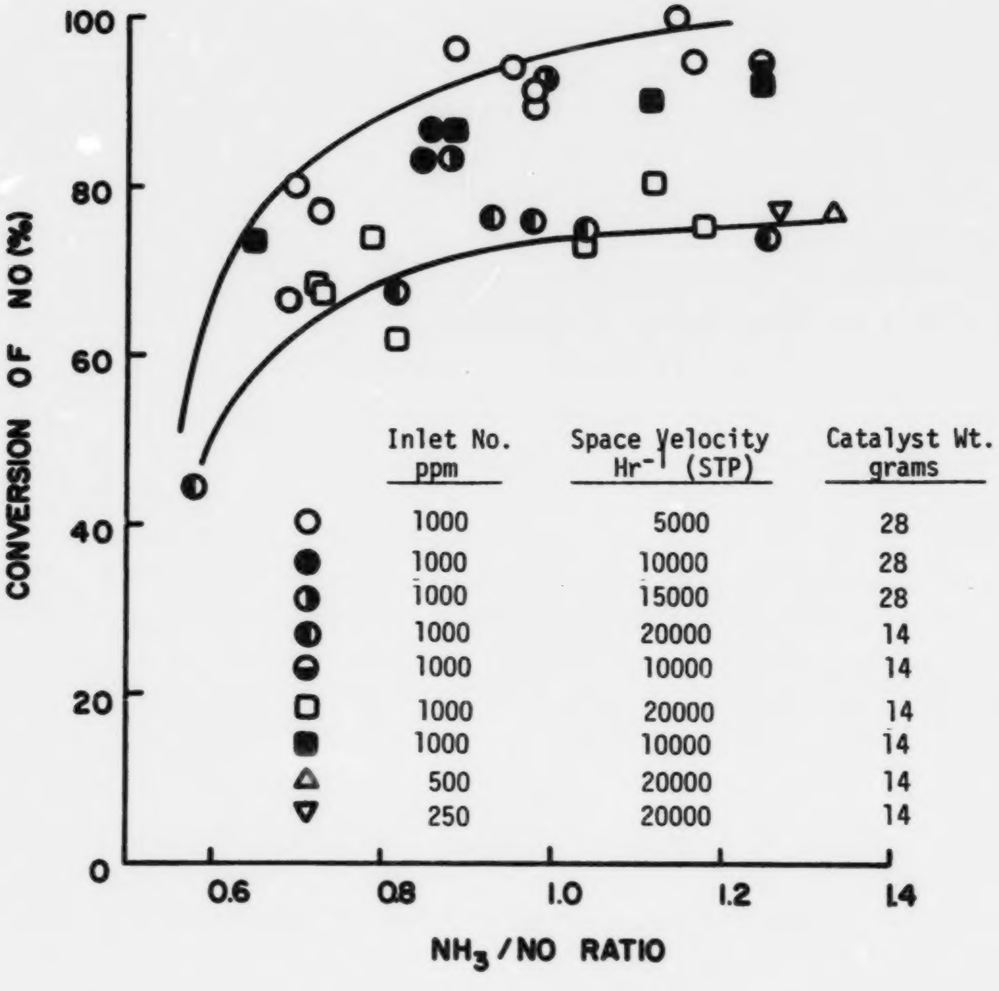

Figure 7. Reduction of NO with NH_3 on Fe-Cr catalyst at 400°C, 14% CO, 5% H_2O, 3% O_2 present in N_2 carrier.

parameters (inlet NO concentration, catalyst bed size at constant space velocity) had no discernable effect on NO conversion. The NH_3 to NO ratio effect appears to level off at a ratio value of 1 (the stoichiometric value is 0.67) and approaches zero at a value of about 1.2. The effect of space velocity appears to diminish at about 15,000 hr^{-1}. NO reduction in excess of 90% was reproducibly obtained in the presence of 3% oxygen at 400°C, 10,000 hr^{-1} (STP), and greater than 1 NH_3 to NO ratios. The temperature effect is shown in Figure 8; the optimum reaction temperature is shown to be 400 ± 30°C. These catalysts did not promote N_2O production within the experimental range tested and under certain conditions, they decomposed all of the excess ammonia used. Thus, a flue gas stream which was free of NO, H_2O and NH_3 exited the catalyst bed. The SO_2 effect on NO conversion was also investigated. These catalysts were subjected for over 50 hours to synthetic flue gas containing in excess of 1000 ppm SO_2. Selective NO reduction by NH_3 was not affected by the presence of SO_2 at 400°C; the SO_2 was also unaffected.

Figures 9 and 10 present a summary of the parametric investigations performed with commercial vanadia on alumina catalysts (Harshaw, Filtrol). The results are very similar to those obtained with the Fe-Cr oxide catalysts. A slightly larger space velocity effect was observed with these catalysts than with the Fe-Cr oxides and the excess NH_3 was not decomposed on them. They also did not promote N_2O production and they were not affected by the presence of SO_2 in the flue gas stream. In addition to the parameters, the effect of oxygen on selective NO reduction by NH_3 was investigated on this catalyst; the results are indicated in Figure 10. Apparently the oxygen has a positive effect on NO reduction at low temperatures and oxygen concentrations which diminishes as both these parameters increase.

On the basis of the above data and the preliminary cost analysis presented in Section 5, the Fe-Cr oxides and vanadia catalysts appear to be definite candidates for utilization in power plants as the means of NO_x abatement. It should, however, be noted that this conclusion was based on very preliminary data; substantial experimental work is needed before these catalysts are considered ready for power plant adaptation (especially long-term data on physical and chemical stability and scale-up performance).

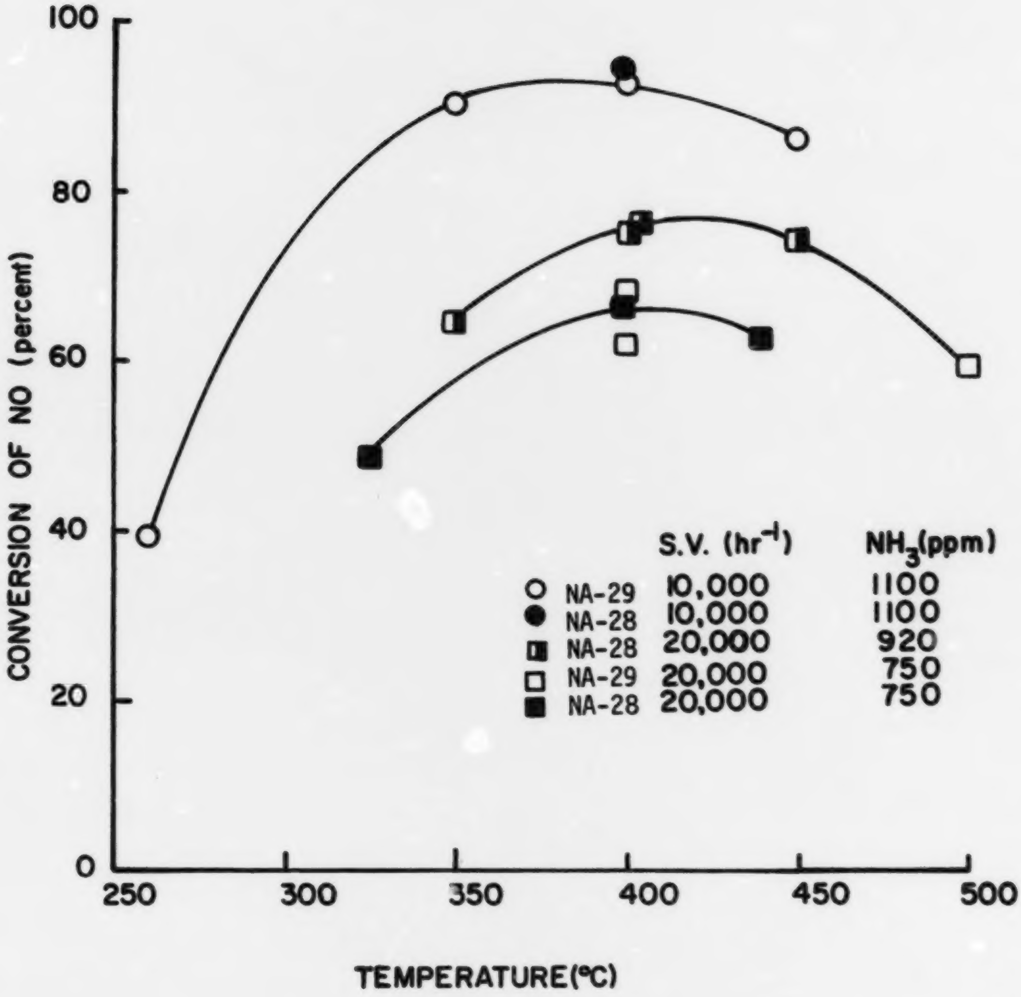

Figure 8. Effect of Temperature on Selective NO Reduction by NH_3; Fe-Cr Oxide Mixture Catalysts

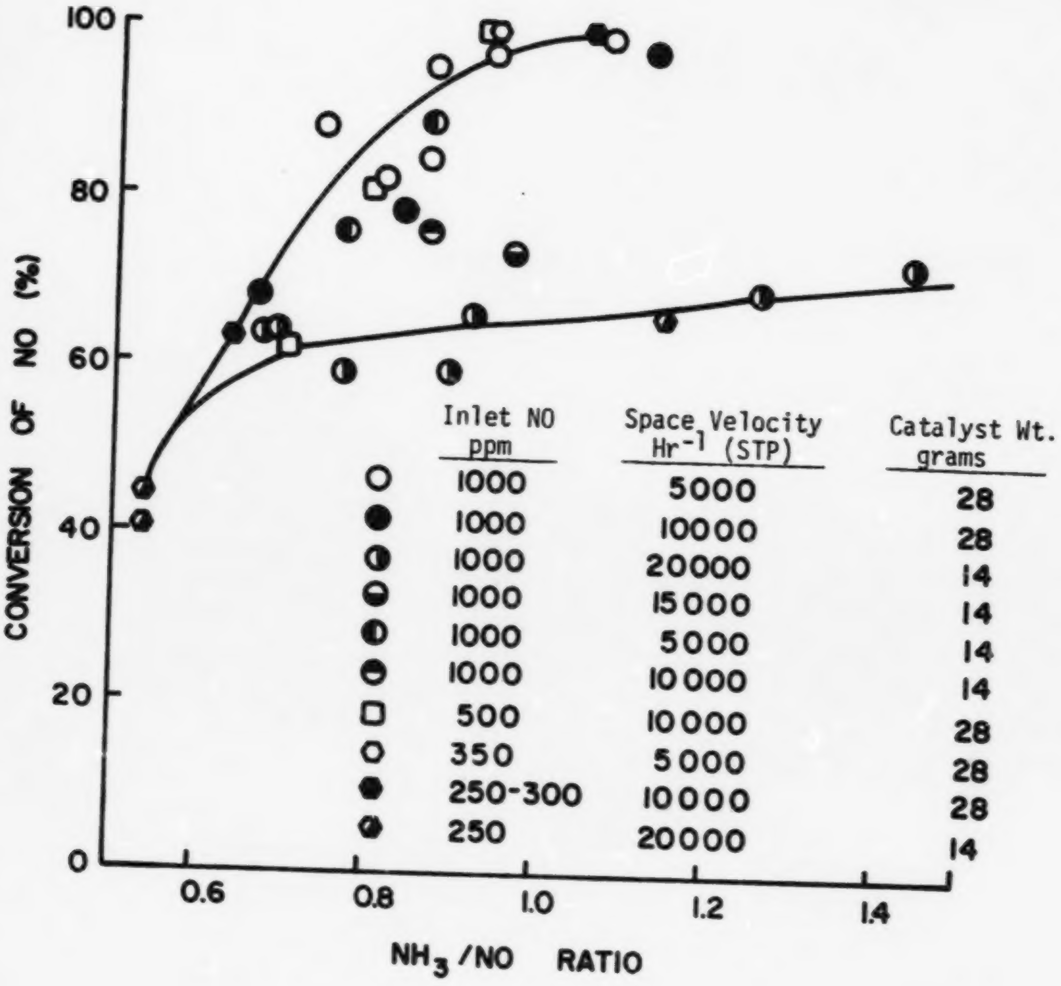

Figure 9. Reduction of NO with NH$_3$ on V_2O_5 catalyst at 400°C, 14% CO_2, 5% H_2O, 3% O_2 present in N_2 carrier.

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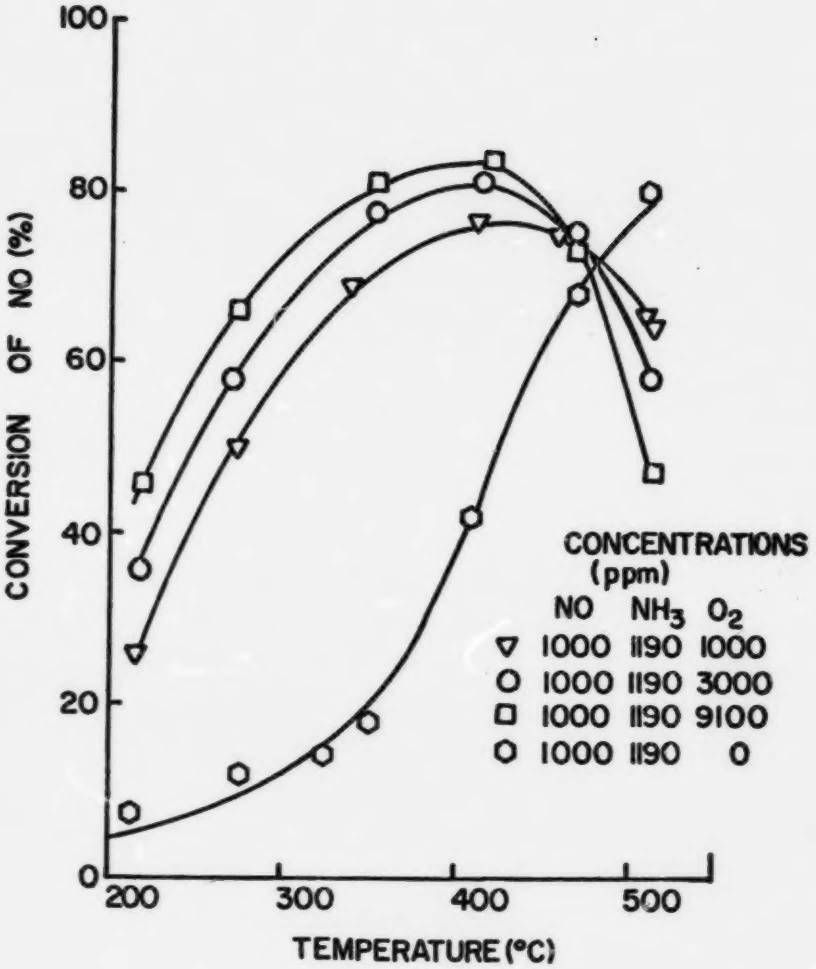

Figure 10. Temperature and Oxygen Effect on Selective NO Reduction by Ammonia; Vanadia Catalysts

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The parameters investigated on the two catalysts discussed above were also studied with 0.5% Pt on alumina; pertinent data is given in Figure 11 The effect of NH_3 to NO ratio was similar to that observed with non-noble metal catalysts. Space velocity up to 20,000 hr^{-1} (STP) had no effect on NO reduction; NO conversion was also not affected by NO concentration in the range of 250-1000 ppm. The temperature effect (not shown) was similar to that observed with the non-noble metal catalysts except that the maximum in NO reduction occurred at approximately 250°C (150 degrees below that of the non-noble metal catalysts). Substantial quantities of N_2O were produced with this catalyst and the excess ammonia was not decomposed although some of it was converted to N_2O. The difference in behavior with respect to N_2O production and NH_3 decomposition or oxidation between Pt and non-noble metal catalysts may be due to the reaction temperature (250 vs 400°C). This latter parameter appears to be responsible for the SO_2 effect observed with platinum. An immediate loss of activity for NO reduction was observed with Pt when 1000 to 3000 ppm SO_2 was added to the synthetic flue gas stream at 209°C. At 250°C a gradual loss of catalytic activity was observed over an 18 hour period. In both cases the catalyst was completely regenerated by passing air through it at 400°C. During the early stages of regeneration SO_3 evolution was observed indicating that salt deposition had previously occurred on the catalyst.

The low temperature and high space velocity render Pt an attractive catalyst for the selective NO_x reduction by NH_3. Its cost and to a lesser extent the N_2O production are drawbacks that could possibly be tolerated; its deactivation by SO_2, however, excludes its use with flue gases containing SO_2. It is, of course, conceivable that if the flue gas contains only a few ppm SO_2 the Pt catalyst can remain sufficiently active for several days or even weeks before it requires regeneration; it is, however, believed that the frequency of regeneration will be higher than that for power plant maintenance. This shutdown implies the need for a second catalyst bed, or a part of it. The latter requirement could render Pt unattractive because of cost.

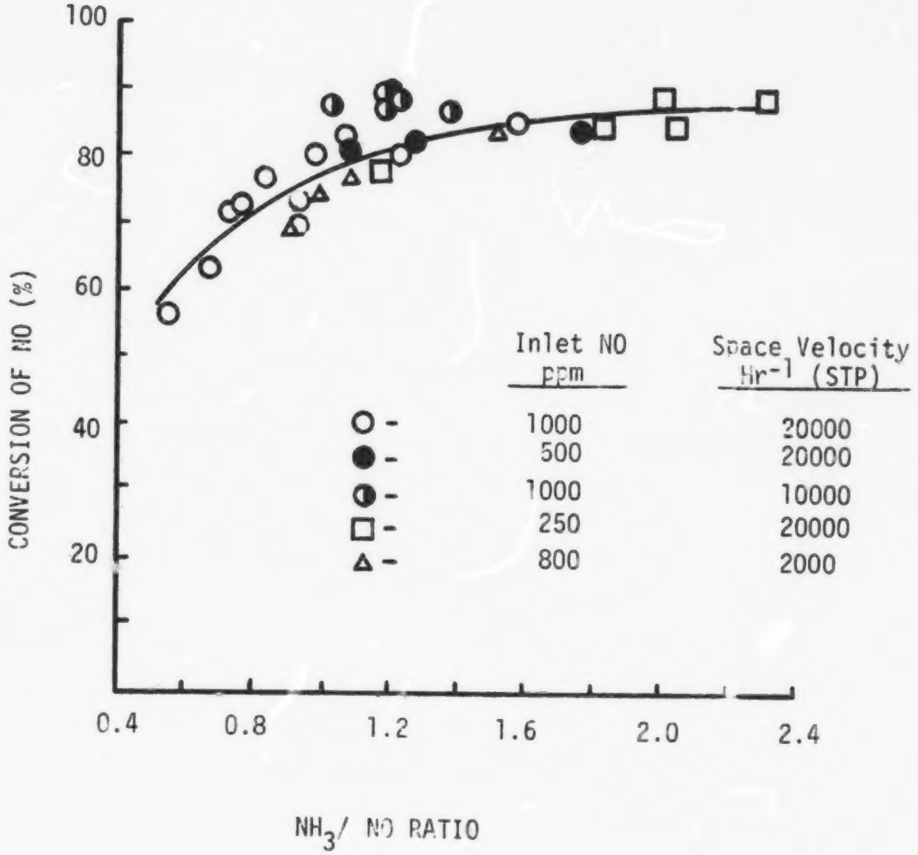

Figure 11. Reduction of NO with NH_3 on Pt catalysts, 250°C, Synthetic Flue Gas (14% CO_2, 5% H_2O, 3% O_2 in N_2).

Very recently, Hitachi Ltd. of Japan[47] has begun operation of an NO_x abatement pilot plant utilizing the selective NH_3-NO process promoted by a zirconium doped lanthanum-copper oxide catalysts (Table 12). The pilot plant operates at a power plant flue gas flow rate of about 100 m^3/min (3500 SCFM) and at a space velocity of approximately 25,000 hr^{-1}. Preliminary results indicate that maximum NO reduction occurs at 300°C with SO_2 free flue gas; reportedly, higher temperatures are required when SO_2 is present. Actual NO_x conversion data was not available at this writing. From what is known to date, this catalyst appears to be even more promising than the Fe-Cr oxides and vanadia catalysts (higher space velocity operation).

3.3 NONSELECTIVE CATALYTIC REDUCTION OF NO - SIMULTANEOUS NO_x-SO_x ABATEMENT

Nonselective catalytic NO_x reduction has been investigated in conjunction with NO_x abatement of three sources: automobiles (IC engines), nitric acid plants, and power generating plants (large combustion sources). The large majority of these investigations relate to the first two sources; however, the data and conclusions derived from them can be of value to NO_x control in power plant flue gas provided proper extrapolations are made.

Nonselective NO_x reduction implies that sufficient reductant is present in the flue or exhaust gas streams to reduce all the oxidant constituents of the stream, principally O_2, SO_2 and NO_x. The reductants are either generated in the burner or engine by fuel rich combustion or are added to the combustion stream; cost consideration limits the choice of additives to H_2, CO, and hydrocarbons. Reductant generation during combustion is possible with IC engines and probably with natural gas-and oil-fired burners. Reductant must be added (separately generated) to coal-fired power plant flue gas and nitric acid plant tail gas.

Nonselective NO_x reduction catalysts, especially non-noble metal catalysts, behave differently with reductant rich gas generated at the combustion source than with gases of the same reductant-oxidant stoichiometry (i.e. rich) to which the reductant was added later. NO_x reduction in the former gas streams occurs at lower temperatures and somewhat higher space velocity than in the latter. The principal reason is the difference in oxygen concentration of the catalytic reactor inlet stream. Rich or near stoichiometric combustion permits only low quantities of oxygen into the combustion gases, part or all of which reduces to CO_2 prior to reaching the catalyst. Lean combustion gases and nitric acid plant tail gases contain substantial quantities of oxygen which normally do not react with the added reductant prior to reaching the catalyst bed. Thus, care must be exercised in data extrapolations from automobile exhaust NO_x control investigations to power plant application. Also, in a reducing environment sulfur compounds can be severe catalytic activity poisons and data on NO_x reduction derived from sulfur-free gas mixtures should not be extrapolated to combustion gases from sulfur containing fuels. It is principally for these reasons that catalysts which proved successful for NO_x abatement in IC engine exhausts or nitric acid plant tail gas are not as efficient or they are inappropriate for power plant use.

Control of NO_x by nonselective reduction on noble metal catalysts has been well developed for nitric acid tail gas. Such schemes are presently in use and could be adaptable to power plants using sulfur-free fuel. Very low sulfur fuel may be used if a small excess of oxygen is present in the reactor (oxygen inhibits platinum poisoning). However, the present cost of sulfur free or nearly sulfur-free fuel, the scarcity of natural gas and the cost of noble metal catalysts mitigate against this approach. Selective reduction by ammonia on non-noble metal or even noble metal catalysts would be a more preferable approach; non-noble metal catalysts in the selective process would probably be operated at the same temperature and space velocity values as Pt or Pd in the nonselective process for the same extent of NO_x reduction. The use of the nonselective process in nitric acid plants was justified because of the relatively low volume of gases to be treated, high NO_x concentrations, and clean fuel availability at low cost (in the past). Even for these sources, however, serious thought is given to conversion to the selective ammonia reduction process. Further discussion of the nonselective reduction processes as applied to tail gases (Pt, Pd catalysts) is not warranted. Several descriptions of these schemes and data on them can be found in the papers cited in the subject index printout under the keywords "noble metal catalysts" or "nonselective reduction"; a brief discussion of these processes is also given by Bartok et al.[2]

Non-noble metal catalysts have been proven active promoters of nonselective NO_x reduction, even in the presence of oxygen and sulfur, provided the reductant-oxidant stoichiometry ratio in terms of equivalents was at 1. Most of the investigations, which are substantial in number, were performed in conjunction with NO_x control in automobile exhaust. No attempt is being made here to review the individual studies on catalytic NO_x reduction. Data summaries on many of them are given by Bartok,[2] Shelef,[3] Yolles,[48] Caretto,[49] and Perrine and Limin;[50] a comprehensive index of the individual studies can be found in the printouts of Volume II of this report. The aim here is to summarize the types of catalysts claimed to be efficient in nonselective NO_x reduction, to outline the conditions under which activity was evident, and to present in more detail catalysts and schemes that appear promising for simultaneous NO_x-SO_x reduction. This approach is taken from the conviction that nonselective reduction schemes adapted to power plants should be capable of substantially removing both NO_x and SO_x.

A host of non-noble metal catalysts have been claimed efficient NO-CO, NO-H_2, or NO-hydrocarbon reaction promoters at temperatures as low as 200-300°C and space velocities in excess of 10,000 hr^{-1} (STP). Most of these claims are based on NO-reductant-diluent systems. As the gas mixture constituents approach power plant flue gas composition (CO_2, H_2O, O_2 and SO_2 present) the NO reduction temperature rises, space velocities drop, and the promising catalyst list becomes shorter. Copper based catalysts, rare earths, certain transition metals and mixtures of the above head the list of active catalysts for nonselective NO_x reduction. Some of them, e.g., copper based catalysts, promote the simultaneous NO_x-SO_x reduction to N_2 and S_n, respectively.

The operating conditions of the catalyst (temperature, space velocity) depend on the type and source of reductant, the reductant-oxidant ratio, and flue gas composition (CO_2, H_2O, SO_2, and especially the quantity of O_2 to be reduced on the catalyst). Investigations in ICE-exhaust control reveal that a number of non-noble metal catalysts can reduce NO_x in near stoichiometric exhaust at temperatures below 427°C (800°F) and space velocities in excess of 15,000 hr^{-1} (STP); higher temperatures were required for complete conversion. Under the present contract (Task 2) over 30 catalysts were screened for nonselective NO reduction activity with H_2 and CO. An SO_2-free synthetic flue gas was used at 20,000 hr^{-1} space velocity and 400°C. All the non-noble metal catalysts proved inactive; the Pt and Pt-Mo catalysts showed good activity. These tests and the data derived from them are presented in Section 4 of this report. It is doubtful that lower space velocities (e.g., 10,000 hr^{-1}) would have proven any of the non-noble metal catalysts efficient at reducing NO_x nonselectively at temperatures at or below 400°C. In fact it does not appear that an efficient non-noble metal catalyst has been identified for use in nonselective simultaneous NO_x-SO_x reduction at about 10,000 hr^{-1} (STP) and below 538°C (1000°F). At lower space velocities non-noble metal catalysts have been reported efficient near 427°C (800°F), which appears to be the upper desired temperature limit for power plant application.

Ryason and Harkins[51] (Chevron Research) were one of the first teams to investigate simultaneous NO_x-SO_x reduction with CO on non-noble metal catalysts at low space velocities (2,000 to 4,000 hr^{-1} STP) in the 500°C temperature regime. Typical data obtained with copper oxide on alumina catalysts and with dry synthetic flue gas are given in Table 14 below.

Table 14. SIMULTANEOUS REDUCTION OF SO_2 AND NO_x BY CATALYZED REACTION WITH CO: COPPER-ON Al_2O_3 CATALYST, 538°C (1000°F), REACTANTS IN N_2

Reactant Concentration				Residence time, sec	Percent Reduction, SO_2	Apparent Percent Reduction, NO_x
SO_2, %	CO, %	CO_2, %	NO_x, ppm			
0.47	1.3	8	∿125	0.57	98	78-100
0.47	1.3	8	∿125	0.46	98	31-100
0.47	0.97	5.8	∿160	0.57	95	100

Part of the SO_2 in these experiments was reduced to COS; the majority was reduced to elemental sulfur. Using thermodynamic data these investigators calculated that the maximum elemental sulfur recovery possible in flue gases similar to the above at 538°C would be 77% of the SO_2 present and it will occur at CO concentrations which are stoichiometric with respect to NO_x and SO_2 in the gas mixture. The above investigators attempted to obtain the same type of data with flue gas from an oil-fired boiler operated on the fuel rich side of stoichiometry. These attempts failed to generate quantitative data because of mechanical difficulties; the presence of elemental sulfur, however, indicated that SO_2 conversion was taking place.

Ryason and Harkins concluded that simultaneous NO_x-SO_x reduction by CO on Cu, Ag, and Pd catalysts was technically feasible; they suggested that the COS production, though not desirable, should not be a problem because of the low concentrations involved when near stoichiometric quantities of CO are used. There was no mention of H_2S formation. According to Ryasen and Harkins the required reductant (CO) can be generated at the burner by slightly rich fuel/air operation. This suggestion appears impractical and possibly undesirable for power plant adaptation. In general, it is difficult to operate burners near stoichiometric air-to-fuel ratios with the required degree of stability to produce CO within a narrow ppm range (excessive generation of CO will cause the production of large quantities of COS, plus the fact that CO is a pollutant itself); certain fuels, e.g., coal, can not be burned efficiently without excess air; finally, generation of reductant rich flue gas at burner temperatures may cause partial reduction of SO_2 to sulfur species which can then react with boiler tubing to form sulfides, thus reducing their life-span. It would appear that reductant addition or reductant generation in a two stage type combustion is indicated for this type of process adaptation to power plants.

Similar but more extensive catalytic NO_x-SO_x reduction studies with CO on non-noble metal catalysts have recently been performed at the University of Massachussetts, Chemical Engineering Department Laboratories (partially EPA sponsored project). Quinlan et al.[52] reported on data obtained with a commercial alumina-supported copper oxide catalyst (Harshaw 0803) and with synthetic flue gases. The data was generated at the 400-425°C (753-796°F) temperature range and at space velocities of 6,000 to 8,000 hr^{-1} (STP); larger than stoichiometric quantities of CO were used in all the tests. Typical results are shown in Table 15.

The data indicates virtually complete NO reduction to nitrogen but only a maximum of 62% conversion of SO_2 to elemental sulfur when both pollutants (SO_2 and NO) were present. Higher SO_2 conversions to elemental sulfur were attained in the absence of NO. Between 15-20% of the reduced SO_2 was converted to COS. Attempts to increase SO_2 reduction by increasing the reductant to oxidant ratio (CO concentration) or by increasing residence time (lower space velocities) increased the production of nonrecoverable gaseous sulfur species, principally COS. Figures 12 and 13 illustrate this point. Figure 12 shows COS production as a function of SO_2 reduction; Figure 13 shows the noncollectable sulfur species (other than elemental sulfur species in the catalytic reactor effluent) as a function of SO_2 reduction. These investigators report that neither H_2S nor NH_3 were detected in the reactor effluent during these investigations.

The same groups have been working with other catalysts most of which are proprietary. During a telephone communication with Professor Kittrel (head of the group) we were informed that one of the proprietary catalysts they are working on proved to be much more efficient in the promotion of simultaneous NO_x-SO_x reduction than CuO; neither the nature of the catalyst nor data generated on it has become available to us. It is, however, our understanding that even this catalyst promotes COS production and possibly H_2S.

The Kittrel group also investigated Fe-Cr oxide catalysts one of which was Girdler G3A. Reportedly, it was one of the more active NO_x-SO_x reduction catalysts. The catalyst screening studies performed during this program did not indicate so. Copper oxide showed higher activity than G3A. Neither catalyst was very active under screening test conditions (400°C, 20,000 hr^{-1}) for nonselective NO reduction with CO and H_2. It is true, however, that test conditions to which Kittrel and UCLA subjected

Table 15. DATA FOR REDUCTION OF SO_2 AND NO BY CARBON MONOXIDE ON SUPPORTED CuO[52]

Temperature °C	Upstream Composition, ppm			Contact Time, Sec	Conversion, %		% COS Production
	CO	SO_2	NO		SO_2	NO	
425	6140	2190	293	0.178	72.0	97.7	10.5
425	6060	2250	990	0.178	40.9	94.5	9.2
425	5750	2190	0	0.230	92.4	-	11.6
410	6060	2250	995	0.228	36.9	83.2	11.6
410	6060	2250	1005	0.228	41.7	92.0	12.0
410	5830	2210	352	0.228	63.9	97.0	11.5
410	5830	2210	0	0.228	73.1	-	12.2
401	6320	2160	0	0.228	82.9	-	11.0
401	6160	2255	400	0.229	62.1	100.0	11.3
401	6624	2200	908	0.229	43.1	96.6	12.6
400	6560	2200	0	0.229	73.7	-	11.8

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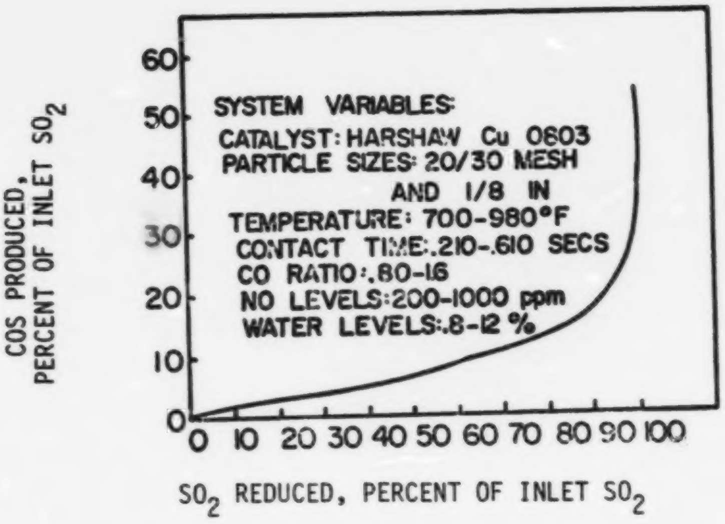


Figure 12. COS Production as a Function of SO_2 Reduction on CuO Catalyst[52]

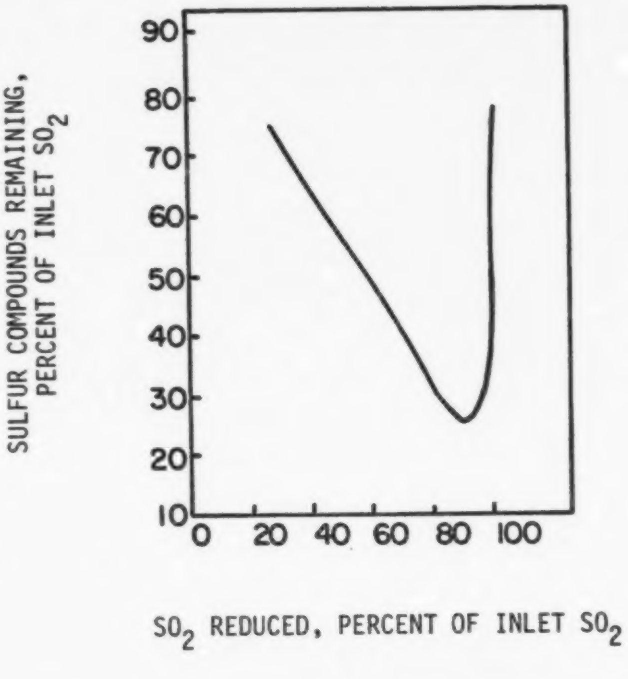


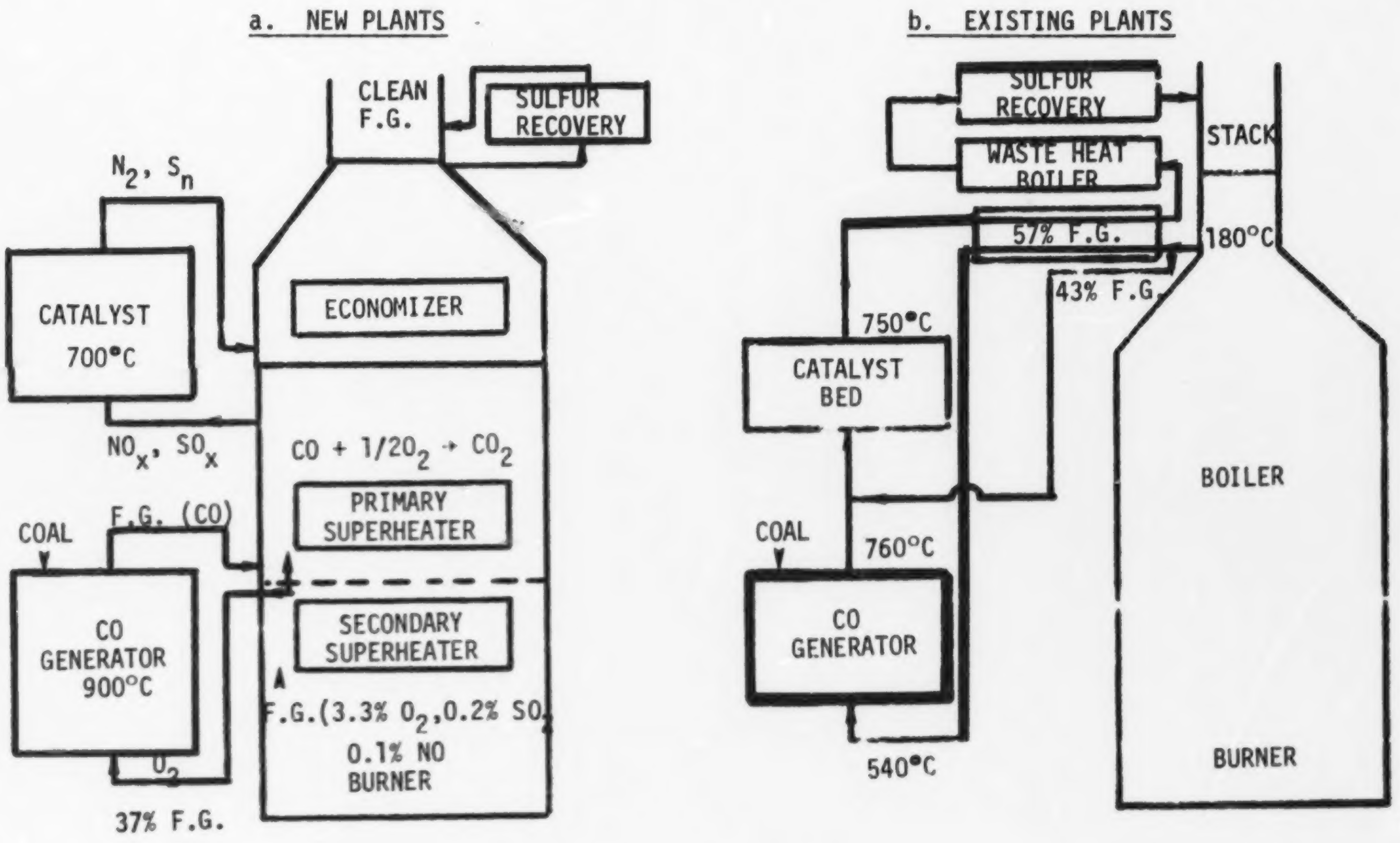
Figure 13. Residual Sulfur Species in Flue Gas Reduced on CuO Versus Extent of SO_2 Reduction 52

G3A were substantially different that comparison may be unfair. Actual data from the Kittrel group on G3A was not made available to us.

In 1970, TRW investigated the Harshaw 0803 catalyst (10% CuO on alumina) for activity in NO_x-SO_x reduction with CO; this is the same catalyst reported by Quinlan et al. Under the TRW test conditions (higher temperature and space velocity) both H_2S and COS were produced in the synthetic flue gas stream to which CO was added in stoichiometric amounts with respect to oxidants present (O_2, NO, SO_2); COS production, however, was substantially lower than that observed by Quinlan. It is possible that this catalyst promoted the water-gas shift reaction at the higher temperatures TRW used (600-700°C), but did not promote it at the temperatures used by the University of Massachusetts groups (~400°C). Otherwise, the data can be considered comparable when extrapolated.

TRW selected the above catalyst as a potential candidate for the simultaneous catalytic NO_x-SO_x process conceptually depicted in Figures 14a and 14b. In Figure 14a, which depicts the process as envisioned adapted to new power plants, a portion of the flue gas (30-40%) at the secondary superheater is diverted through a coal-fed reductant generator. The reductant rich (CO, H_2) generator effluent returns to the boiler where complete oxygen reduction occurs homogeneously and the generated heat is absorbed by the boiler. Under proper conditions of reductant generator operation (size, residence time, temperature) the boiler flue gas at this point should only contain the quantity of CO required to reduce the SO_2 and NO_x constituents of the flue gas. The entire flue gas steam is passed over the selected NO_x-SO_x reduction catalyst where NO_x is reduced to N_2 and SO_2 to elemental sulfur; then it goes through the economizer, sulfur collector, air preheater and to the stack.

Even though a preliminary review of the scheme in Figure 14a by Combustion Engineering Company suggested it to be feasible for existing power plants, the scheme in Figure 14b is more likely to be the preferred one for existing power plants. This scheme differs from that of Figure 14a in the following aspects: the flue gas is treated downstream of the air preheater. Over 50% of the flue gas is diverted through the CO generator, which is operated at


a. NEW PLANTS
CLEAN F.G.
SULFUR RECOVERY
N2, Sn
CATALYST 700°C
ECONOMIZER
NOx, SOx
CO + 1/2O2 → CO2
PRIMARY SUPERHEATER
COAL
F.G. (CO)
CO GENERATOR 900°C
SECONDARY SUPERHEATER
F.G.(3.3% O2,0.2% SO2
0.1% NO
BURNER
O2
37% F.G.
b. EXISTING PLANTS
SULFUR RECOVERY
WASTE HEAT BOILER
STACK
57% F.G.
180°C
43% F.G.
750°C
CATALYST BED
BOILER
COAL
760°C
CO GENERATOR
540°C
BURNER

- SV = 1,500 HR^{-1} (STP) IN CO GENERATOR; 9,000 HR^{-1} (STP) IN CATALYST BED
- NO_x REDUCTION: COMPLETE
- SO_x REDUCTION: ~80%

Figure 14. TRW Simultaneous Catalytic NO_x-SO_x Reduction By Coal Process

lower temperatures. Part of the oxygen in the undiverted flue gas stream would probably convert to CO_2 on the catalyst. The energy from the coal fed to the CO generator must be absorbed by either a waste heat boiler or a gas turbine for the production of additional power.

Proof-of-principle tests on the scheme depicted in Figure 14a were performed under TRW funding in 1970. Typical data is shown in Table 16. A preliminary cost analysis on both schemes was performed under Task 3 of this program and the results are presented in Section 5. The capital costs for adopting these schemes to 800 MW plant were estimated at 7.3 and 15 million for new and existing power plants, respectively; the operating costs were less than one mil per KWH in both cases. In the above cost estimates it was assumed that a single-stage catalytic treatment would be sufficient to meet clean air requirements. This presupposes either that the catalytic reactions can be optimized to minimize H_2S and COS production or a different catalyst can be identified which would not promote the production of these pollutants.

Reportedly a catalyst capable of simultaneously reducing NO_x-SO_x by CO without H_2S or COS production has been identified by researchers at NYU (New York University). The catalyst (AL 30873) is proprietary and its composition was not revealed to us. However, Professors Hnatow and Happel,* principal investigators on the process, sent us the data shown in Table 17. The data was generated on two catalysts. One of the catalysts (AL 21773) promoted the production of H_2S but not COS; the second (AL 30873) did not promote either.

If additional testing, especially long term tests, validates the data in Table 17, simultaneous catalytic NO_x-SO_x reduction could prove to be the most desirable abatement process for power plant adaptation.

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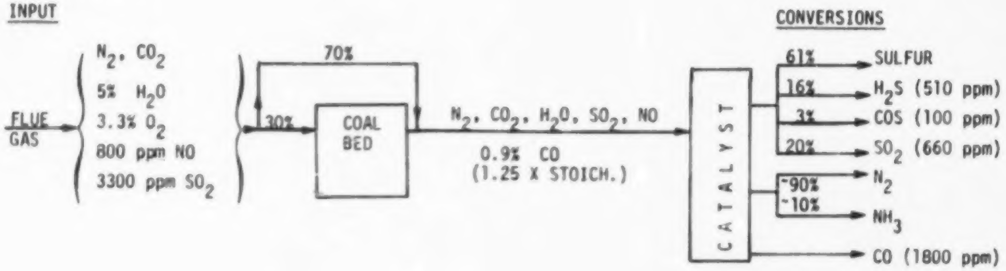
* Presently not with NYU.

Table 16. TYPICAL STEADY STATE NON-OPTIMIZED RESULTS ON TRW'S NO_x-SO_x CATALYTIC REDUCTION PROCESS

DATA SET NO. 1

INPUT

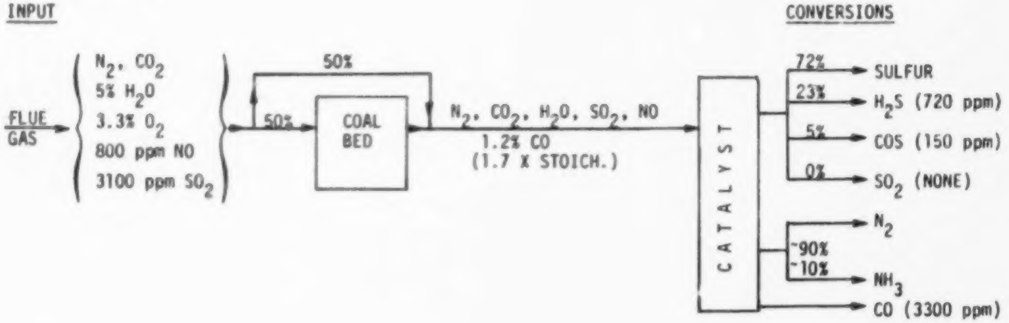

FLUE GAS
N_2, CO_2
5% H_2O
3.3% O_2
800 ppm NO
3300 ppm SO_2
70%
30%
COAL BED
N_2, CO_2, H_2O, SO_2, NO
0.9% CO
(1.25 X STOICH.)
CATALYST
CONVERSIONS
61%
SULFUR
16%
H_2S (510 ppm)
3%
COS (100 ppm)
20%
SO_2 (660 ppm)
~90%
N_2
~10%
NH_3
CO (1800 ppm)

CONDITIONS:

CATALYST TEMPERATURE - 1280 ±30°F
RESIDENCE TIME - 0.40 SECONDS AT S.C.
PRESSURE - ATMOSPHERIC
CATALYST - 10% COPPER ON ALUMINA
CATALYST BED SIZE - 18.7 CC (CORRESPONDING TO 110 $FT^3/10^6FT^3$F.G./HR)
COAL TEMPERATURE - 1740°F
COAL BED SIZE - 43 CC(CORRESPONDING TO 260 $FT^3/10^6FT^3$F.G./HR)
FRACTION OF F.G. THROUGH COAL BED - 30%

DATA SET NO. 2

INPUT


FLUE GAS
N_2, CO_2
5% H_2O
3.3% O_2
800 ppm NO
3100 ppm SO_2
50%
50%
COAL BED
N_2, CO_2, H_2O, SO_2, NO
1.2% CO
(1.7 X STOICH.)
CATALYST
CONVERSIONS
72%
SULFUR
23%
H_2S (720 ppm)
5%
COS (150 ppm)
0%
SO_2 (NONE)
N_2
~90%
~10%
NH_3
CO (3300 ppm)

CONDITIONS:

SAME AS FOR EXAMPLE NO. 1 EXCEPT

- COAL TEMPERATURE - 1690°F VS 1740°F
- COAL BED SIZE - 45 CC (CORRESPONDING TO 260 $FT^3/10^6FT^3$F.G./HR) VS 43 CC
- FRACTION OF F.G. THROUGH COAL BED - 50% VS 30%

Table 17. CATALYTIC NO_x-SO_x REDUCTION BY CO ON NYU CATALYSTS

Catalyst No.	Feed Composition, Mole %					Space Velocity, Hr^{-1}	Temp °C	Length of Run, Hours	Conversions % of Feed		COS/SO_2 %	H_2S/SO_2 %
	SO_2	NO	CO	H_2O	He				SO_2	NO		
AL 21773	1.0	0	1.9	3.0	Balance	5,250[a]	520	12	95[b]	-	0	40
						10,500[a]	520	12	95[b]	-	0	37
						21,000[a]	520	12	95[b]	-	0	30
AL 30873	1.0	1.0	2.7	3.0	Balance	10,500[a]	520	7	85[b]	100	0	0

[a] These are actual space velocities; the STP values are approximately 65% lower.

[b] Maximum possible conversion; CO completely reacted.

A modified version of the simultaneous catalytic NO_x-SO_x reduction process has been recently advanced to the pilot plant scale in Japan by the Hitachi Ship Building Company.[1] The pilot plant is capable of treating 170 SM^3/min (5900 SCFM) flue gas drawn from the Sakai Refinery, Kansai Oil Company. Complete NO_x reduction to N_2 is claimed and the SO_2 concentration in the catalytic reactor effluent is reportedly less than 10 ppm. Figure 15 is a block diagram of the process which was originally developed by Chevron Research Company.

Flue gas is divided into two portions. The larger portion of the split stream is heated to 850°C. The hot gas is used to heat manganese-iron sulfite, formed in the SO_2 absorption step. Manganese ferrite (regenerated absorbent) is sent to the SO_2 absorber (dotted line). The SO_2 expelled is used for manufacture of H_2SO_4. The flue gas stream is mixed with the regeneration bypass stream and passed through a CO generator containing coke. After dust elimination and SO_2 absorption, the gas is passed through a catalytic converter containing cupric oxide catalyst.

The process as shown could be adapted to either existing or new power plants and it does not have the H_2S-COS production problem; therefore, it appears promising. However, proper process assessment requires additional operational data which was not available to us as of this writing. A process drawback may be the high regeneration temperature of the absorbent.

As an extention to its NO_x-SO_x catalytic reduction process TRW has conceived a modified NO_x-SO_x scheme, labeled the TRW Sulfide Process. The process can be considered as a catalytic-regenerative scheme capable of complete and simultaneous NO_x-SO_x abatement. The process concept is depicted in Figure 16. In this scheme simultaneous NO_x-SO_x reduction occurs in the CO generator; therefore, a second stage reactor (e.g., CuO catalyst) is not needed. The entire flue gas is diverted at the secondary superheater to the coal bed (CO generator) where the SO_2 of the flue gas is reduced to elemental sulfur, H_2S, and possibly COS. The reduced sulfur species react with iron, fed to the CO generator with the coal, to form sulfides. The latter are removed with the ash for possible regeneration. Simultaneously, the NO_x is

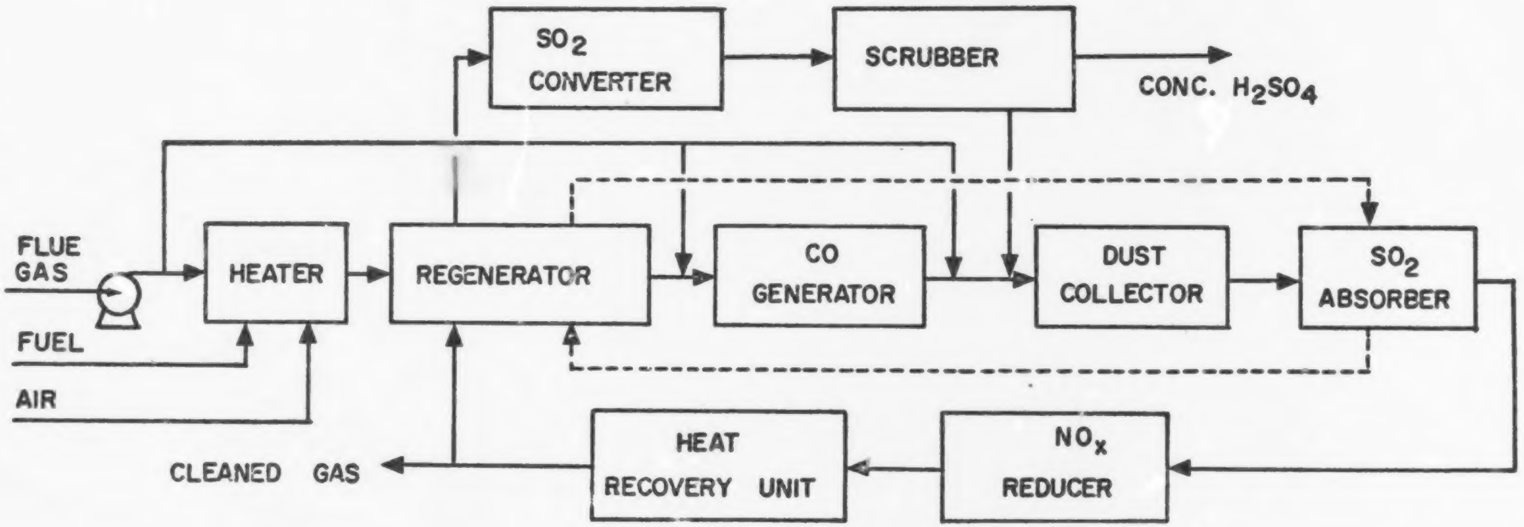

FLUE GAS
FUEL
AIR
HEATER
REGENERATOR
SO_2 CONVERTER
SCRUBBER
CONC. H_2SO_4
CO GENERATOR
DUST COLLECTOR
SO_2 ABSORBER
NO_x REDUCER
HEAT RECOVERY UNIT
CLEANED GAS

Figure 15. NO_x-SO_x Abatement by the Chevron Hitachi Process [1]

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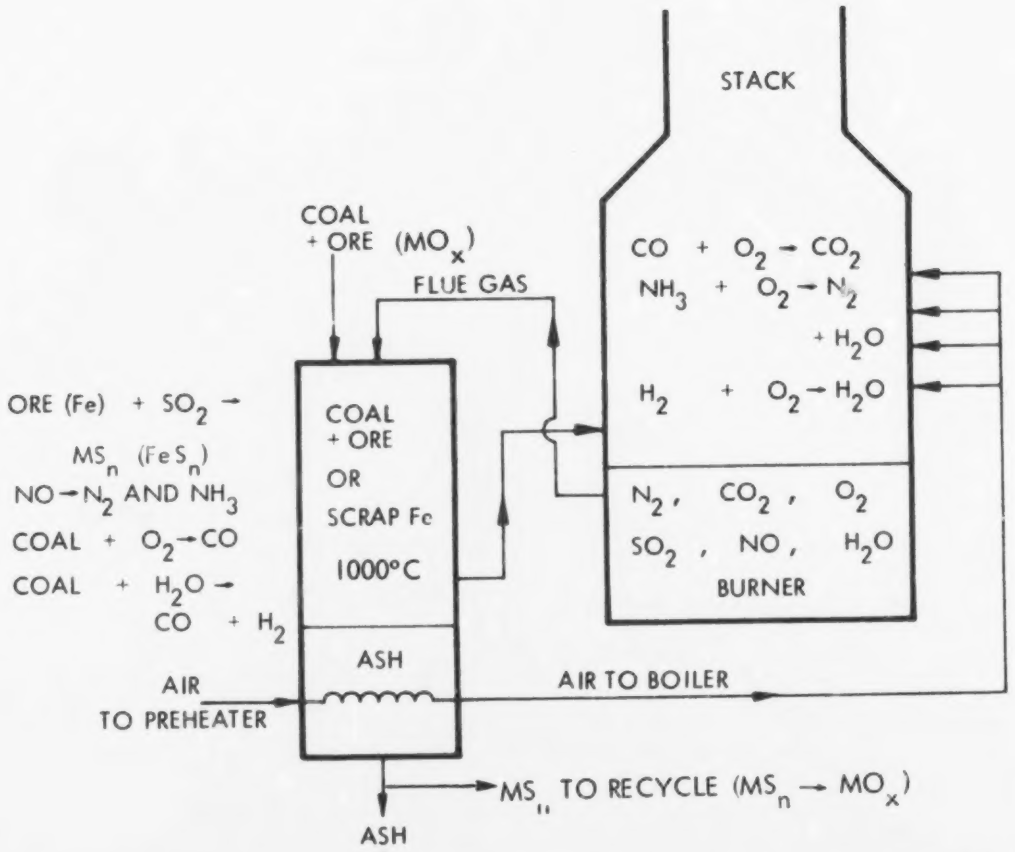
STACK
CO + $O_2 \rightarrow CO_2$
NH_3 + $O_2 \rightarrow N_2$ + H_2O
H_2 + $O_2 \rightarrow H_2O$
N_2, CO_2, O_2
SO_2, NO, H_2O
BURNER
COAL + ORE (MO_x)
FLUE GAS
ORE (Fe) + SO_2 → MS_n (FeS_n)
NO → N_2 AND NH_3
COAL + O_2 → CO
COAL + H_2O → CO + H_2
COAL + ORE OR SCRAP Fe
1000°C
ASH
AIR TO PREHEATER
AIR TO BOILER
MS_n TO RECYCLE ($MS_n \rightarrow MO_x$)
ASH

- MO_x REPRESENTS A NUMBER OF OXIDE OR CARBONATE ORES; HOWEVER, PROOF-OF-PRINCIPLE DATA EXISTS ONLY WITH SCRAP IRON.
- COAL FEED RATE TO BURNER: 220 TONS PER HOUR.
- COAL FEED RATE TO GASIFIER (SECONDARY COAL): 100 TONS PER HOUR
- IRON FEED RATE: 14 TONS PER HOUR (ASSUMING FeS TO BE THE PRODUCT)
- POWER PLANT CAPACITY: 800 MW
- SPACE VELOCITY: 1,500 HR^{-1} (STP)
- COMPLETE NO_x AND SO_x CONVERSION TO N_2 AND FeS, RESPECTIVELY.

Figure 16. NO_x-SO_x Abatement by the TRW Sulfide Process reduced to N_2 (it has not been established if any of these reactions are catalyzed by the ash or iron present in the CO generator). The CO generator effluent gas, rich in reductants (CO and H_2) and free of O_2, NO_x, and sulfur compounds, is returned to the boiler at approximately the same temperature it left (the CO generator operates nearly isothermally because of competing endothermic, e.g., CO_2 reduction, and exothermic, e.g., oxygen and water reduction, reactions with coal). Preheated air is added to the boiler for the complete oxidation of the reductants to CO_2 and water; the generated heat is absorbed by the boiler in the normal manner.

Limited proof-of-principle data with synthetic flue gas (14% CO_2, 5% H_2O, 3.3% O_2, 3000 ppm SO_2, 800 ppm NO) revealed total SO_2 and NO removal with this process. Also the oxidation of the reductants in a simulated boiler was complete. The experiments were performed at 920 ± 20°C (∿1700°F) and 1,500 hr^{-1} space velocity. The coal bed size was approximately 50 cc; the coal was mixed with 2.5% of its weight iron in the form of wire. Iron consumption was approximately equal to 15 wt. % of the coal consumption in the CO generator indicating FeS formation rather than FeS_2.

The process in Figure 16 was costed on the basis of the scan proof-of-principle data described above (two tests were performed). The estimated capital cost for process adaptation to a new 800 MW power plant was estimated at $5 million; the operating cost was estimated at 2 mils per KWH. Details on this cost analysis are presented in Section 5 of this report. A large fraction of the operating costs resulted from the iron consumed in the process ($100 per ton) and not regenerated. It is believed that less expensive reactants than iron can be used in the CO generator (e.g., iron oxide, dolomite, or even coal ash) as sulfur getters. It is also believed that the majority of these sulfur-getters can be regenerated, if desirable.

The Sulfide Process as depicted in Figure 16 is adaptable to new power plants only since the required boiler changes for adaptation to existing plants will be substantial. However, a scheme similar to that presented in Figure 14b may render this process adaptable to existing power plants.

3.4 CATALYTIC OXIDATION OF NITRIC OXIDE

Oxidation of NO to NO_2 is desirable because NO_2 can be easily removed from power plant flue gas in a variety of wet-scrubbing processes as nitrites, nitrates, or complex salts. Equimolar mixtures of NO-NO_2 are also removable by the above processes;[2] thus, complete NO to NO_2 conversion is not required.

The nitrogen oxides in power plant flue gases are virtually all NO so that some degree of oxidation is required before the wet-scrubbing processes can be utilized for NO_x abatement. Homogeneous oxidation of NO at the flue gas or wet-scrubber conditions is impractically slow. Two catalytic approaches have been tried in an effort to improve NO_x scrubbing efficiency. One involves gas phase NO oxidation, the other liquid phase oxidation. Neither has proven successful to date, at least not for power plant flue gas treatment. Some promise, however, has been indicated by at least two processes involving liquid phase catalytic oxidation. The available data, or at least the data available to us, are not sufficient for firm process assessment; thus, the labeling of these processes as promising is only tentative.

One of these processes is the Continuous Catalytic Absorption Process depicted in Figure 17 as applied to nitric acid plant tail gas. Mayland and Heinze[53] describe the process as a catalytic oxidative absorption operation. The nitric acid tail gas is passed countercurrently with dilute nitric acid over a catalytic packing which promotes the oxidation of NO to nitric acid; the acid is recovered. According to the authors this process is more efficient and more cost-effective that the nonselective gas phase catalytic processes presently used (Section 3.3)

Attempts to obtain information concerning the catalyst and the process operating conditions failed to yield results. According to the authors (telephone communication) additional information on the process will be released upon completion of pilot plant and full scale plant development presently underway. A pilot plant unit is scheduled to operate on an ordnance nitration plant tail gas. Before a definite conclusion can be drawn concerning potential applicability of this process to power plant

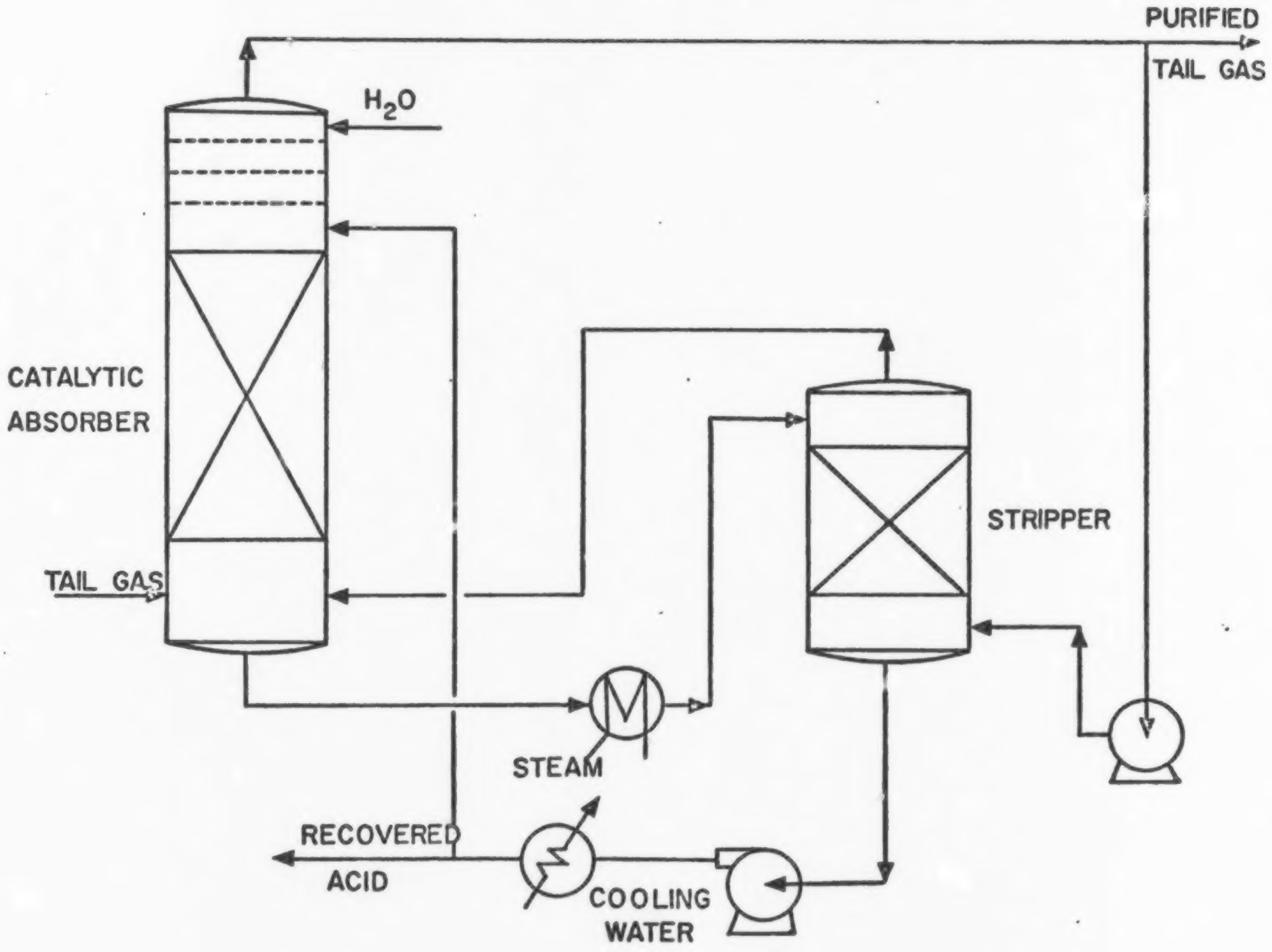
PURIFIED
TAIL GAS
H_2O
CATALYTIC
ABSORBER
TAIL GAS
STRIPPER
STEAM
RECOVERED
ACID
COOLING
WATER

Figure 17. Continuous Catalytic NO_x Absorption Process[53]

flue gas it is necessary to know at least the space velocity required for efficient process operation and if NO_2 must be present in the tail gas prior to processing.

A second process with potential NO_x scrubbing capabilities is the TRW "OXNOX" Process. This is also a catalytic oxidative scrubbing process which utilizes hypochlorides (or chlorine) to convert NO to nitrates. Key to the process efficiency and cost effectiveness is the presence of NO_2 in the flue gas prior to entering the scrubber. This constituent is the process catalyst which promotes oxidation in the scrubber. Proof-of-principle experiments indicated that it must represent at least 5% of the NO_x present in the flue gas prior to entering the scrubber. Virtually complete NO_x scrubbing was attained under practical operating conditions when 10 ppm NO_2 was present in a synthetic flue gas containing 420 ppm NO.

Figure 18 depicts the envisioned power plant adaptation scheme for the TRW "OXNOX" Process. The catalyst for NO-SO_2 oxidation step in the diverted flue gas stream has not been identified as yet. Neither the literature survey nor the screening tests performed under this program (Task 2) revealed an efficient catalyst for NO oxidation. However, certain charcoals[2] and rare earth-vanadium oxide mixtures (Task 2) may be sufficiently active for the "OXNOX" Process because of the small fraction of the flue gas requiring catalytic treatment in the gas phase (very low space velocities become practical).

It should be noted that the "OXNOX" Process is being proposed as a "total pollutant abatement process" (NO_x, SO_2, Hg, Sb, PNA, etc.).

3.5 TASK 1 CONCLUSIONS AND CANDIDATE CATALYST SELECTION

The information reviewed in Task 1 led to the conclusions and candidate catalyst selections presented below:

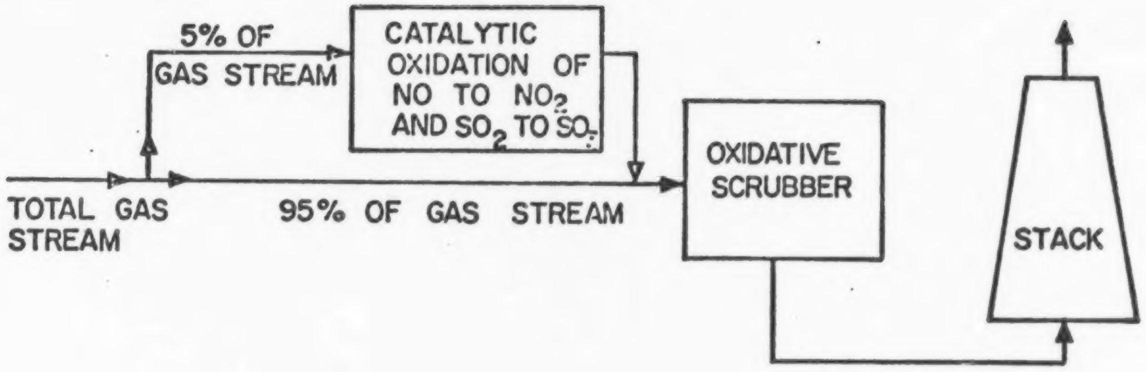
5% OF GAS STREAM
CATALYTIC OXIDATION OF NO TO NO_2 AND SO_2 TO SO_3
TOTAL GAS STREAM
95% OF GAS STREAM
OXIDATIVE SCRUBBER
STACK

Figure 18. TRW "OXNOX" Oxidative Scrubbing Process

- NO$_x$ Decomposition. The available data in the literature indicates limited success in the identification of an efficient catalyst for NO$_x$ decomposition. Platinum, copper oxide, and vanadia have shown some potential for NO decomposition at low space velocities, but they have not been tested on power plant flue gas. These three catalysts were selected as prime candidates for screen-testing with simulated power plant flue gas in Task 2.

- Selective NO$_x$ Reduction. No catalysts were identified as efficient promoters of the selective reduction of NO with either H_2 or CO. Several catalysts have been shown or claimed to be effective promoters of the selective reduction of NO with NH_3; however, data on them generated with actual or simulated power plant flue gas are virtually nonexistent. The following catalysts were selected for screening selective NO reduction potential under Task 2: Pt, Pt-Mo, Mo, rare-earth oxides, WO_3, V_2O_5, Fe and Cr oxides, and Fe on graphite.

- Nonselective NO$_x$ Reduction. Noble metals appear to be the most effective nonselective NO$_x$ reduction catalysts, but only in sulfur-free flue gases. Non-noble metal catalysts (e.g., CuO, Fe and Cu chromates) require at least 500°C temperature for effective activity; however, these catalysts can be efficient in the presence of sulfur containing flue gas. Hydrogen, carbon monoxide, and hydrocarbons are suggested as reductants (gaseous fuels). The nonselective reduction approach would be desirable for power plant adaptation only as a simultaneous NO$_x$-SO$_x$ abatement process (reductant and adaptation costs would be unjustifiably high to be used as an add-on to a desulfurization process or to a power plant using sulfur free fuel).

Available data on simultaneous NO_x-SO_x catalysts are adequate for preliminary engineering analysis, provided the assumption is made that a second reactor is not required for abatement of product H_2S or COS (gaseous SO_2 reduction products formed on most nonselective reduction catalysts).

A representative simultaneous NO_x-SO_x catalytic reduction process was selected for preliminary design and cost analysis. Also, CuO and a number of transition metal based catalysts were selected for screening with H_2 and CO containing synthetic power plant flue gas with the objective of identifying a nonselective NO_x reduction catalyst effective at temperatures below 400°C.

- NO Oxidation. It was not possible to identify an effective NO oxidation catalyst during the literature review. Certain types of charcoal were suggested as promising NO oxidation catalysts at low space velocities. Such catalysts would be inappropriate for utilization in high gas volume NO_x sources, e.g., power plants. The required large bed volumes and the potential for high attrition render these catalysts undesirable. Rare-earth oxides, vanadia, and tungsten oxide have also been suggested as possible NO oxidation catalysts, but the available data on them was insufficient for assessment; they were selected for screening under Task 3.

3.6 POTENTIAL HAZARDOUS PRODUCTS OF CATALYTIC NO_x ABATEMENT SCHEMES

Experience has shown that catalytic activity and catalyst integrity depend greatly on the chemical nature of the catalyst, the method of its preparation, the chemical composition of the environment which it is being subjected, and the reaction parameters. In the air pollution control area, loss in activity can cause excessive emissions in the pollutant being controlled as well as emissions of any air polluting additives injected into the stream for the catalytic conversion of the original pollutant. Loss of catalytic integrity (physical or chemical) can result in particulate emissions or in emissions of hazardous catalyst-flue gas reaction products. In addition, a catalyst may promote side reactions under certain operational conditions whose products may be detrimental to the environment.

Catalysts proposed for NO_x abatement may not be immune to the problems described above. As indicated earlier, concern has been raised over side reactions producing H_2S and COS. Production of metalic carbonyls by the reaction of CO with certain catalysts (monel, nickel, iron, manganese, and even noble metals) have been mentioned as concerns. Particulate generation due to catalyst errosion or attrition is always a concern. Sulfur poisoning of certain catalysts is a potential problem.

The validity of the above concerns can not be assessed unless detailed data are available on the particular catalytic scheme proposed for power plant adaptation. In the ensuing paragraphs an attempt is made to indicate potential problems that may be encountered with each of the proposed principal methods of NO_x abatement (decomposition, reduction, oxidation), to assess probabilities of problem occurance, and, when possible, to present potential remedies. This analysis is based on extrapolated and in most cases incomplete data and it should be considered only tentative.

- NO_x Decomposition Schemes. The biggest concern with this scheme is low catalyst efficiency under practical temperature and space velocity conditions. Platinum appears to be the most effective catalyst. Platinum is subject to sulfur poisoning in reducing atmospheres, but there has not been any indication that it is poisoned by SO_2 in an oxidizing atmosphere at NO_x decomposition conditions. Decomposition catalysts could, in principle, promote NO oxidation to NO_2 or N_2O_4 if the reactor is operated at low-to-moderate temperatures (<400°C); however, platinum does not appear to promote NO_2 formation at NO decomposition temperatures and we know of no other catalyst which is effective in NO decomposition at temperatures where NO_2 is stable. Should NO_2 be formed, it can easily be scrubbed in an alkali scrubber.

- Selective NO_x reduction with NH_3 (other reductants are not considered here because of low effectiveness). The primary concern with this group of catalysts is long term effectiveness (emissions of residual NO_x and NH_3). Platinum may present a problem with SO_x containing flue gas. This catalyst appears to be "poisoned" by ammonium sulfate decomposition; however, it can easily be regenerated by hot gas (approx. 300°C gas). Its use with sulfur containing flue gas depends on economics and the latter depend on the concentration of SO_2 in the flue gas. Sulfur dioxide does not appear to be a problem with the non-noble metal catalysts proven effective in selective NO_x reduction; however, these catalysts are efficient at 400°C while platinum has optimum activity at 200°C. Platinum promotes N_2O formation, but this nitrogen oxide is not considered a pollutant at present. Formation of NO_x or N_2O_4 does not appear to be promoted by any of the catalysts proposed for this scheme. Formation of H_2O_2 is a question mark, although its formation is highly unlikely at 400°C.

- Nonselective NO_x Reduction. The most likely reductant to be used in this scheme is CO or a combination of CO and H_2 (coal derived reductants). This scheme could present severe side reaction problems. A number of catalysts proposed for this scheme promote the production of COS or H_2S or both. These gases are highly toxic and difficult to abate at the concentrations produced. This, of course, is a potential problem only with SO_2 containing flue gases; its magnitude depends on the SO_2 concentration in the flue gas, the particular catalyst used, and the reactor operating conditions. Even though the H_2S/COS problem has surfaced with the majority of the catalysts tested for simultaneous NO_x/SO_x reduction, NYU has reported preliminary data on an effective SO_x/NO_x reduction catalyst which may not promote COS or H_2S formation (see Section 3.3 of this report).

Metal carbonyls have also been mentioned as a concern in schemes involving NO_x reduction by CO. Metal carbonyls may be formed from the reaction of CO with the active metal of the catalyst, with the walls of the reactor, or with trace metals in the flue gas; the biggest concern is reaction with the catalyst. Nickel, iron, manganese, and possibly noble metal carbonyls could potentially form under certain flue gas environments. Nickel carbonyl is the most toxic of the metal carbonyls (0.3 ppb tolerance level in ambient air), but it does not form above 200°C and no nickel containing catalyst has been suggested as an effective NO_x reducing catalyst at such low temperature. The concern over nickel carbonyl arose from the proposed application of monel catalysts for NO_x control in auto-exhaust. It was feared that nickel carbonyl could form during engine start-up (reaction of the CO produced during engine start-up with the catalyst in the afterburner). There is no analogous cituation in a power plant; but even if it were, tests at ESSO[54] proved the concern unfounded. The other three carbonyls are a question mark. They are not as toxic as nickel carbonyl and to our knowledge a tolerence level has not been established for them. In addition, it is not certain that they will form at all or that they would be stable in the atmosphere; however, they should not be dismissed without further investigation.

Incomplete elemental sulfur collection and unreacted CO emissions are additional potential problems of this scheme. Elemental sulfur collection efficiency can be improved by the use of electrostatic precipitators and CO can be catalytically oxidized in a second stage reactor, if necessary. However, both these units will increase the cost of the process.

- Oxidation of NO to NO_2. Hazardous by-products of this scheme have not been identified principally because an effective catalyst for this scheme has not been found.

In addition to the specific scheme and specific catalyst pollutant generation potential there is also the particulate generation problem which could arise from any of the catalysts proposed. Physical and/or chemical degredation of the catalyst could result in unacceptable levels of fine particulates or even mists. However, it should be noted that if the problem is not severe enough to affect catalytic activity, particulate collection can easily be alleviated by electrostatic precipitators.

The candidate catalyst selections for NO_x abatement from power plants presented in the previous section of this report were based on data indicating that these catalysts would probably promote the conversion of NO_x to nonpolluting species under practical operating conditions. The available data were insufficient for assessment of catalyst efficiency, catalyst stability, and extent of possible side reactions. This type of information must be generated during bench scale and pilot plant testing of the promising catalyst selected for use in a specific NO_x abatement scheme. During the catalyst screening studies described in the next section, very preliminary data were generated on catalyst efficiency and stability so as to establish potential; detailed assessment of performance has been scoped for Phase II of this program.

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4. CATALYST SCREENING AND PROOF-OF-PRINCIPLE EXPERIMENTS (TASK 2)

The objective of this task was to screen candidate NO_x abatement catalysts for applicability to power generating plants. These catalysts were selected as potential candidates on the basis of information assembled in Task 1. Only catalysts on which available data was inadequate for either technical or preliminary engineering evaluation were tested.

Catalyst screening and proof-of-principle experiments were performed with simulated, SO_2-free, power plant flue gas nominally at 400°C (752°F) and at 20,000 hr^{-1} (STP) space velocity.*

Catalysts which indicated promise as efficient promoters of NO_x abatement in any of the above processes (decomposition, oxidation, reduction) were further tested for sensitivity to important parameters. Principal parameters varied included temperature, space velocity, and important flue gas component concentrations. In addition, the SO_2 effect on these catalysts was investigated.

The ensuing sections list the screened catalysts and detail catalyst preparation, screening procedures, screening results, and the results of parametric investigations on the promising candidate catalysts.

4.1 CATALYSTS SELECTED FOR SCREENING

The catalysts selected for screening are listed in Table 18. The catalysts are grouped on the basis of predominant active metal and not necessarily in the chronological order of testing; thus, the numbering system differs from that used in interim monthly reports. Suggestions for selection were derived: (a) from previously published work where these or similar catalysts were subjected to gases containing important components of power plant flue gas, (b) from patents where claims of NO_x abatement were made, and (c) from previous research data at TRW and UCLA.

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* Unless otherwise indicated, space velocities throughout this report are given as the ratio of flue gas volume flow rate at standard conditions per hour to the volume of the catalyst used.

Table 18. LIST OF CATALYSTS SUBJECTED TO SCREENING TESTS

Catalyst No.	Principal Active Element(s)	Composition (Type[a])	Source
NA-1	Pt	0.5% Pt on alumina	Engelhard
NA-2	Pt	New batch of NA-1	Engelhard
NA-3	Mo, Pt	22.2% Mo, 0.1% Pt on alumina (1/16 inch spheres)	TRW
NA-4	Mo, Pt	NA-3 pressed into cylinders[b]	TRW
NA-5	Mo	27% Mo on alumina (pressed[b])	TRW
NA-6	Mo	14.7% Mo on alumina	UCLA
NA-7	Mo	NA-6 reduced in H_2 at 480°C	UCLA
NA-8	Mo	NA-6 reduced in H_2 at 700°C	UCLA
NA-9	Mo, Co	15% MoO_3, 2.7% Co_3O_4 on alumina	Filtrol
NA-10	R.E.	Rare earth oxides (refined ore, pressed)	Molycorp
NA-11	R.E., Co	15% R.E. cobalt oxide on alumina (pressed)	UCLA
NA-12	R.E., Pb	NA-11 doped with 10% Pb[c]	UCLA
NA-13	Gd, Mo	15% $Gd_2(MoO_4)_3$ on alumina (pressed)	UCLA
NA-14	Gd, Mo	15% Gd MO_3 on alumina (pressed)	UCLA
NA-15	Gd, V	15% Gd VO_3 on alumina (pressed)	UCLA
NA-16	La, Co	15% $LaCoO_3$ on alumina	UCLA
NA-17	Cu	16.5% CuO on alumina	UCLA
NA-18	Cu, Pb	NA-17 doped with 1% Pb[c]	UCLA
NA-19	Cu, Pb	NA-17 doped with 5% Pb[c]	UCLA
NA-20	Cu, Pb	NA-17 doped with 10% Pb[c]	UCLA
NA-21	W	13.1% W on alumina (20 x 30 mesh)	TRW
NA-22	W	NA-21 pressed into pellets	TRW
NA-23	W	10% WO_3 on alumina	Harshaw
NA-24	V	10% V_2O_5 on alumina	Filtrol
NA-25	V	10% V_2O_5 on alumina	Harshaw
NA-26	Fe, Cr	80% Fe_2O_3, 7% Cr_2O_3, 1.6% graphite, 0.4% MgO, 0.2% SiO_2[d]	Girdler
NA-27	Fe, Cr	Similar composition to NA-26 (second sample)	Girdler
NA-28	Fe, Cr	10% $Fe_2O_3 \cdot Cr_2O_3$ (83%·17%) on alumina	UCLA
NA-29	Fe, Cr	NA-28 composition (different salts)	UCLA
NA-30	Fe, Cr	56.7% Fe_2O_3, 6.7% Cr_2O_3m 1.4% CrO_3, 35.2% Al_2O_3 (pressed)	UCLA
NA-31	Cr	15% Cr_2O_3 on alumina (pressed)	UCLA
NA-32	Fe	15% Fe_2O_3 on alumina (pressed)	UCLA
NA-33	Fe	15% Fe_2O_3 on alumina	UCLA
NA-34	Fe	20% Fe_2O_3 on alumina	Harshaw
NA-35	Fe, C	Fe on graphite chips (organic impregnation)	UCLA
NA-36	Fe, C	Fe on graphite chips (aqueous impregnation)	UCLA

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[a] Unless otherwise stated the catalysts were prepared by impregnation of performed 1/8 x 1/8 inch alumina cylinders.

[b] Pressed catalysts made by dry-mixing active material with alumina and forming into 1/8 x 1/8 inch cylinders.

[c] Pb-doped catalyst made by impregnation of base catalyst with $Pb(NO_3)_2$ solution and calcining.

[d] Balance unspecified.

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The active catalyst elements belong principally to the transition metal and rare earth groups with platinum, copper, lead and graphite being the only other elements screened. Every attempt was made to include in the screening task representative catalysts from those classes for which NO_x abatement potential had been reported, provided the following criteria were met:

- The candidate catalyst indicated potential for utilization at temperatures below 427°C (800°F).
- The available data indicated that the catalyst could physically survive the power plant flue gas conditions (e.g., flow rates at practical space velocities, temperature, impurities).
- The available data were not sufficient to infer the catalyst's potential for utilization in power plant NO_x abatement. If adequate data were available or the available data could be safely extrapolated, the catalyst was not screened.

It is apparent that the criteria used are somewhat subjective and as a result the above list may not be as comprehensive as intended. One group of catalysts intentionally restricted, because of cost, was the noble metals; the only catalyst investigated from this group was platinum. One batch of platinum (NA-1) was screened in order to generate baseline data for comparison purposes. Platinum was also tested for SO_2 effects on its activity and parametrically scanned for NO decomposition potential. In addition, two preparations of a molybdenum-platinum catalyst (NA-3 and NA-4) were screened to determine the effect of Mo on the Pt activity in the selective reduction of NO by NH_3 (temperature of maximum conversion). The temperature of maximum NO reduction by NH_3 acquires special importance when SO_2 is present in the flue gas stream (platinum activity is severely inhibited by sulfate deposition at temperatures below approximately 300°C).

As a rule, the individual catalysts in Table 18 were selected as potential candidates for one of the outlined NO_x abatement processes (decomposition, oxidation, selective and nonselective reduction); however, most of them were subjected to the eight tests (Section 4.3) designed to screen catalytic activity toward all processes envisioned as practical for power plant use.

4.2 CATALYST PREPARATION

A number of the catalysts screened for NO_x abatement potential were prepared by TRW or UCLA as indicated in Table 18. The following paragraphs detail the methods of preparation of the individual catalysts (those not commercially available).

In general, the screened catalysts were prepared by either impregnation of carrier material with salts of the desired active ingredients or by pressing the powdered carrier (Al_2O_3) with the active metal oxide or oxides. The following list outlines the procedure used with each catalyst.

NA-3 - This catalyst was prepared by soaking 35 g of a UOP platforming catalyst containing approximately 0.1% Pt on Al_2O_3 (1.6 mm spheres) with a 75 ml solution of ammonium molybdate (41 g/100 ml). The unused solution was decanted off and the catalyst was dried and then reduced in H_2 for 4 hours at 700°C.

NA-4 - A sample of NA-3 was ground with 5% stearic acid (used as a die lubricant) and pressed into 3.2 x 3.2 mm (1/8 x 1/8 in) cylinders. The stearic acid was burned out by calcining in air at 500°C for 16 hours.

NA-5 - This catalyst was prepared by the NA-3 procedure except that 115 g of Reynolds 14-20 mesh Al_2O_3 and 175 ml of the ammonium molybdate solution were used.

NA-6 - This catalyst was prepared by the NA-3 procedure except that 35 gm of Filtrol Grade 86 Al_2O_3 (3.2 x 3.2 mm cylinders) was used as carrier. Instead of reduction the catalyst was calcined in air at 480°C for 18 hours.

NA-7 - A sample of NA-6 was reduced at 480°C in H_2 for 20 hours.

NA-8 - A sample of NA-6 was reduced at 700°C in H_2 for 4 hours.

NA-10 - Fifteen grams of bastnasite, a mixture of rare earth oxides (Molycorp; see Table 19) was ground with 85 gm of Al_2O_3 (Filtrol Grade 90) and 5 gm of stearic acid and pressed into 3.2 x 3.2 mm cylinders. The pellets were calcined at 500°C in air for 16 hours.

NA-11 - A mixture of rare earth oxides (American Potash and Chemical Corporation; see Table 19) was ground with cobalt carbonate in a preparation such that the molar ratio of cobalt to each rare earth was unity. The mixture was calcined in air for 20 hours at 1000°C. Compound formation with the general perovskite formula, $(R.E.) \cdot CoO_3$, has been verified for La, Gd, Pr, and Nd in individual tests. Fifteen grams of the resultant mixed oxide was mixed with 85 gm Al_2O_3 and pressed into cylinders as described for NA-10.

NA-12 - Twenty-five grams of NA-11 were impregnated (to total solution take up) with 7.5 ml of a solution containing 4 gm of $Pb(NO_3)_2$. The catalyst was calcined in air at 500°C for 16 hours.

Table 19. APPROXIMATE COMPOSITION OF RARE EARTH OXIDE MIXTURES

Percentage as Oxides	Rare Earth Oxide (American Potash and Chemical Corp.)	Bastnasite (Molycorp)
CeO_2	45.6	27.6
La_2O_3	22.8	41.3
Nd_2O_3	16.2	11.6
Pr_6O_{11}	4.7	4.3
Sm_2O_3	2.8	0.4
Gd_2O_3	1.9	0.3
Y_2O_3	0.2	0.3
Other Rare Earth Oxides	0.8	86.2
Total Rare Earth Oxides	95.0	86.2
SO_3	2.0	-
P_2O_5	0.5	0.5
$Na_2O + K_2O$	0.1	1.0
$CaO + MgO$	1.0	0.8
$Fe_2O_3 + Al_2O_3$	1.5	0.1
Fluorine	-	6.0
SrO_2	0.1	-
BaO	-	1.5
SrO	-	0.9
SiO_2	-	3.0

NA-13 - A mixture of 4.6 gm Gd_2O_3 and 6.7 gm $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was dehydrated and then heated at 1000°C for 16 hours. Fifteen grams of the resultant compound $Gd_2(MoO_4)_3$ was mixed with 85 gm Al_2O_3 and pressed into cylinder as per NA-10.

NA-14 - A mixture of 3 gm Gd_2O_3, 0.8 gm Mo, and 1.5 gm $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ was reacted at 800°C in He for 16 hours. A 15/85 (with Al_2O_3) was pressed into cylinders as per NA-10.

NA-15 - A sample of V_2O_3 was made by reducing V_2O_5 in H_2 at 800°C for 16 hours. A mixture of 1.5 gm V_2O_3 and 3.5 gm Gd_2O_3 was heated in He at 900°C for about 72 hours. The material was pressed into cylinders with 85% Al_2O_3 as per NA-10.

NA-16 - A 1:1 (molar) mixture of La_2O_3 and $CoCO_3$ was calcined in air for 16 hours at 1000°C. The compound $LaCoO_3$ was verified by X-ray diffraction. A 15/85 mixture with Al_2O_3 was pressed into cylinders as per NA-10.

NA-17 - Forty-five ml of a solution containing 90.6 gm $Cu(NO_3)_2\cdot 3H_2O$ was impregnated on 150 gm Al_2O_3 pellets (3.2 x 3.2 mm), dried and calcined at 500°C in air for 16 hours.

NA-18 - Thirty-six grams of NA-17 were impregnated with 0.48 gm $Pb(NO_3)_2$ (total take up) and recalcined as per NA-17.

NA-19 - Thirty-five grams of NA-17 were impregnated with 2.4 gm $Pb(NO_3)_2$ and calcined as per NA-17.

NA-20 - Thirty-three grams of NA-17 were impregnated with 4.8 gm $Pb(NO_3)$ and calcined as per NA-17.

NA-21 - This catalyst was prepared by soaking 25 gm Harshaw 20-30 mesh Al_2O_3 in a 30 ml solution containing 7.62 gm ammonium metatungstate. The excess solution was decanted off and the catalyst was reduced in H_2 at 700°C.

NA-22 - A sample of NA-21 was pressed into 3.2 x 3.2 mm cylinders following the procedure described for NA-4.

NA-28 - Impregnated 100 gm Al_2O_3 pellets (3.2 x 3.2 mm) with a solution containing 53.8 gm $Fe(NO_3)_3 \cdot 9H_2O$ and 2.8 gm CrO_3. The pellets were dried and calcined in air at 500°C for 16 hours.

NA-29 - Prepared as per NA-28 except solution contained 25.3 gm $(Fe(NO_3)_3 \cdot 9H_2O$ and 5.70 gm $Cr(NO_3)_3 \cdot 10.8\ H_2O$; 50.4 gm Al_2O_3 pellets were used.

NA-30 - Pressed as per NA-10 a mixture of 34 gm Fe_2O_3, 4 gm cr_2O_3 and 0.8 gm crO_3 with 21.2 gm Al_2O_3.

NA-31 - Pressed as per NA-10 a 15/85 mixture of Cr_2O_3 and Al_2O_3.

NA-32 - Pressed as per NA-10 a 15/85 mixture of Fe_2O_3 and Al_2O_3.

NA-33 - This catalyst was prepared by total impregnation of 32 gm Al_2O_3 pellets (3.2 x 3.2 mm cylinders) with a solution containing 15.2 gm $Fe(NO_3)_3 \cdot 9H_2O$.

NA-35 - This catalyst was prepared by impregnation of 15 gm graphite chips (4 mm diameter x 2 mm thick) with a solution of 12 gm $Fe(NO_3)_3 \cdot 9H_2O$ isopropanol. Isoamyl alcohol was added and the solution boiled for 4 hours. The chips were washed quickly in acetone and dried in air at 180°C.

NA-36 - This catalyst was prepared by impregnating 25.7 graphite chips with a saturated aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. The catalyst was dried in air at 180°C.

4.3 CATALYSTS SCREENING TEST CONDITIONS

Figure 19 is a schematic diagram of the test apparatus used in this phase of effort. A glass manifold enabled mixing of N_2 carrier gas, NO, CO_2, H_2, air (O_2), and CO. Each gas stream was equipped with individual metering valves and bead-type flow meters. For precise measurement of the flow rates of the species used at low concentrations, flow could be diverted prior to entry into the mixing manifold through a soap-bubble flow meter.

The gas mixture passed through a 4 m preheater coil (6.4 mm diameter stainless steel tube) and into the reactor. Both reactor and preheater were immersed in an electrically heated, fluidized bed furnace containing powdered alundum. The temperature of the fluidized heater was held at the desired level with a meter-relay using a chromel-alumel thermocouple. With the proper air flow rate, the fluidization was sufficient to reduce temperature gradients in the bath to below 5°C.

Water vapor was added to the gas mixture by vaporization of a measured flow of pumped liquid water in a vaporizer tube (1.4 cm diameter x 30 cm long) located immediately upstream of the preheater coil. The vaporizer was heated with electrical tapes to 320-380°C.

Ammonia was fed to the gas stream, when necessary, at the exit of the vaporizer; an analyzed supply of an NH_3-N_2 mixture ($\sim$5% NH_3) was used. In tests for the investigation of sulfur effects, SO_2 (anhydrous) was injected into the gas stream near the point of water admission.

Tests were conducted at a pressure of 4 mm Hg gage which was maintained by regulation of the vent valve. Samples of the reactant effluent streams could be taken through a valving arrangement.

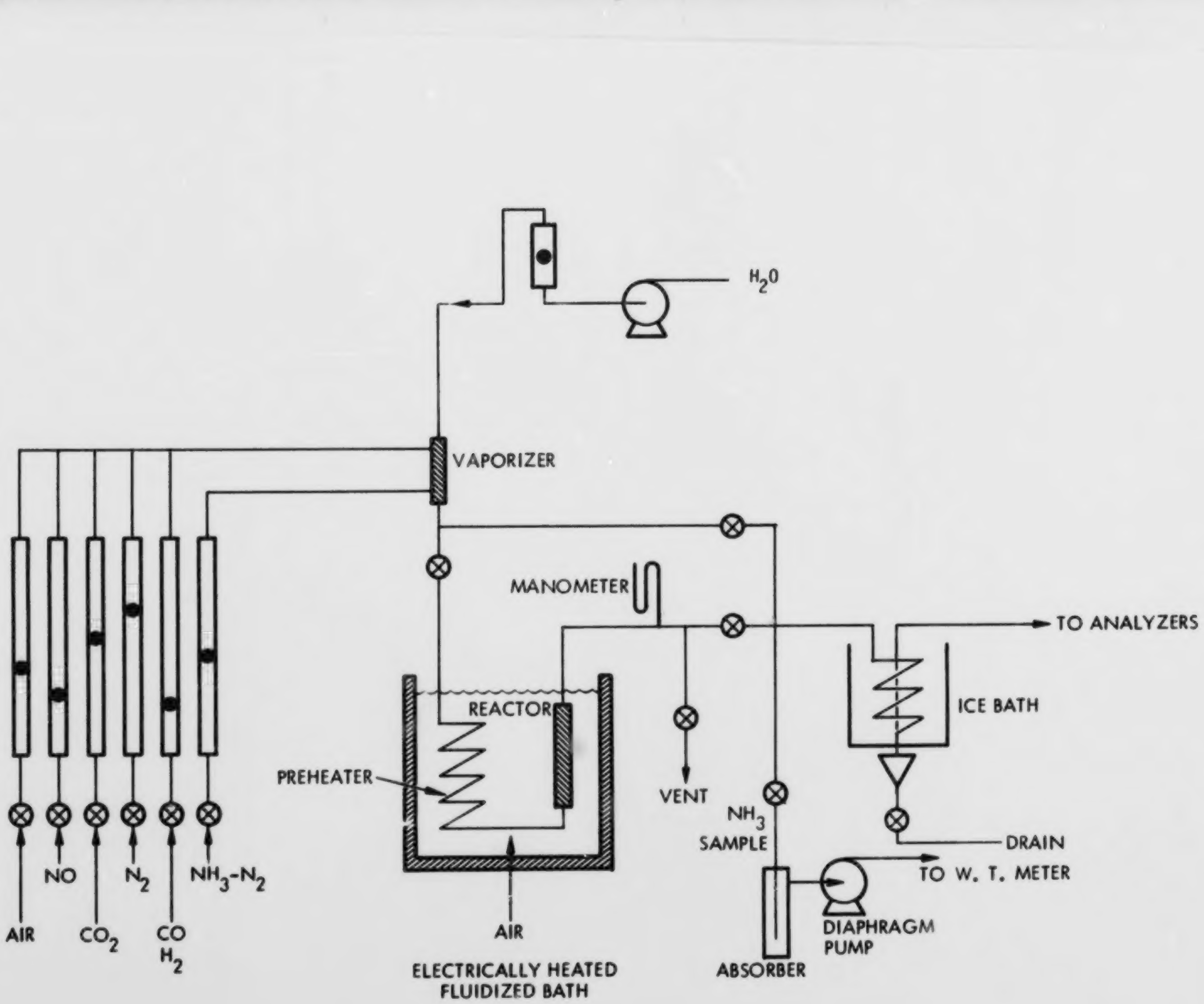
H$_2$0
VAPORIZER
MANOMETER
TO ANALYZERS
REACTOR
ICE BATH
PREHEATER
VENT
NH$_3$
SAMPLE
DRAIN
TO W. T. METER
AIR
NO
CO$_2$
N$_2$
CO
H$_2$
NH$_3$-N$_2$
AIR
ELECTRICALLY HEATED
FLUIDIZED BATH
ABSORBER
DIAPHRAGM
PUMP

Figure 19. Catalyst Screening Test Apparatus

Analyses were performed as follows:

NO	Nondispersive infrared (NDIR) (Beckman Model 315A)
CO_2	NDIR (MSA LIRA 300)
CO	NDIR (MSA LIRA 300)
SO_2	NDIR (MSA LIRA 200)
NO_2	Visible colorimetry (Beckman Model 77 flow colorimeter)
N_2O	Gas chromatography. Perkin-Elmer Model 990 with 3-meter column of Porapak Q and T.C. detector.
NH_3	Absorption in a bubbler of a known quantity of gas (measured with a wet test meter) in 2% boric acid followed by titration with 0.03N HCl using bromocresol green indicator. All lines from the reactor to the bubbler were heated to prevent water condensation. In tests in which SO_2 was present, which interfered with the wet analysis, adsorbed NH_3 was analyzed using a specific ion electrode (Orion).

The reactor used in the screening tests was constructed of stainless steel tubing (1.4 cm diameter x 9 cm long). The catalyst loading was $\sim$14 gm. Standard total flow rate was 283 l/hr (STP) resulting in a space velocity of 20,000 hr^{-1} (STP). The screening tests were performed at 400°C (752°F).

The standard screening test conditions are listed in Table 20 (in a few instances additional isolated points were taken at temperatures other than 400°C and space velocities other than 20,000 hr^{-1}). The rationale behind the test matrix was as follows:

> Test 1 - To determine the potential of the catalyst for promoting the decomposition and/or oxidation of NO in a typical stack gas. In general, Test 1 was always performed first; since an overall oxidizing atmosphere existed in the flue gas, prereduction of the catalyst was considered unnecessary.

Table 20. CATALYST SCREENING TEST CONDITIONS

Test No.	NO (ppm)	O_2 (%)	CO_2 (%)	H_2O (%)	NH_3 (ppm)	CO (ppm)	H_2 (ppm)	Catalyst Screened for NO_x
1	1000	3	14	5	0	0	0	Oxidation and decomposition (lean combustion)
2	1000	3	14	5	667	0	0	Selective reduction (NH_3) (lean combustion)
3	1000	3	14	5	0	0	1000	Selective reduction (H_2) (lean combustion)
4	1000	0.5	14	5	0	0	1000	Selective reduction (H_2) (near stoichiometric combustion)
5	1000	0.5	14	5	0	0	11000	Nonselective reduction (H_2) (near stoichiometric combustion)
6	1000	3	14	5	0	1000	0	Selective reduction (CO) (lean combustion)
7	1000	0.5	14	5	0	1000	0	Selective reduction (CO) (near stoichiometric combustion)
8	1000	0.5	14	5	0	11000	0	Nonselective reduction (CO) (near stoichiometric combustion)

Nominal Conditions: 400°C, 20,000 hr^{-1} (STP) space velocity.

Test 2 - To determine the catalyst's potential for promoting selective reduction of NO with a near stoichiometric amount of NH_3 in the presence of oxygen.

Test 3 - To investigate the catalyst's potential for selectively promoting the reduction of NO with H_2 in large excess of O_2 (lean combustion).

Test 4 - A second NO-H_2 selective reduction test, but with a smaller excess air (near stoichiometric combustion).

Test 5 - To determine the catalyst's potential for nonselective NO_x abatement with H_2.

Tests 6, 7, and 8 - Analogous to Tests 3, 4, and 5 with CO as the reductant.

Tests 5 and 8 were performed with flue gas containing 0.5% O_2, instead of 3%, in order to avoid large quantities of heat release in the catalyst bed and therefore nonisothermal testing.

The flue gas composition, temperature, and space velocity for these tests were selected because it is believed that they represent realistic process adaptation conditions to power plants while at the same time they facilitated data acquisition and accuracy. It was felt that catalysts which would not exhibit any activity under the selected values of temperature and space velocity had a very remote chance of being active at any other value of these parameters compatible to power plant conditions; a possible exception is NO oxidation. NO oxidation and decomposition tests were performed simultaneously and the selected temperature for them was a compromise. The NO content of the test flue gas was set at a higher value than that normally present in power plant flue gas in order to ascertain measurement accuracy, especially that of products. SO_2 was not included in the screening tests in order to avoid undue complications in data acquisition; the SO_2 effect on the activity of promising catalysts was investigated during the parametric tests.

Extensive variations from nominal conditions were employed with promising candidate NO_x abatement catalysts (Section 4.5). Space velocity variations were accommodated by changes in the standard flow rate, but in certain cases a larger catalyst bed was used (∿28 gm) in a somewhat larger stainless steel reactor (1.9 cm i.d. x 9.8 cm long) than the one previously described.

Prior to catalyst screening tests the empty reactor and preheater coils were checked for catalytic activity. The data in Table 21 indicates that at the nominal screening test conditions the input flue gas constituents were not materially affected by either homogeneous reaction or the empty reactor and preheater coil.

Table 21. RESULTS OF TESTS WITH EMPTY REACTOR

Test No.	Inlet Gas Composition				Outlet Gas Composition				Conv. of NO (%)
	NO (ppm)	NH_3 (ppm)	CO (ppm)	H_2 (ppm)	NO (ppm)	N_2O (ppm)	NO_2 (ppm)	CO (ppm)	
1	974	0	0	0	967	0	0	0	0.7
2	974	>5000[a]	0	0	972	0	0	0	0.2
3	910	0	0	931	891	0	0	0	2.1
5	932	0	0	9780	931	0	0	0	0.1
8	903	0	1087	0	889	0	0	1073	1.6

[a] Initially, stoichiometric NH_3 was admitted. After no reaction was observed the NH_3 content was increased to the indicated large excess.

The catalyst screening test data was generated under steady state conditions. Every effort was made to insure that the data was not affected by transient surface adsorption or surface reaction flue gas interactions with the catalyst. Sufficient quantities of flue gas were passed through the reactor to insure system saturation by even the most dilute component. This procedure also insured saturation of the analytical instrument manifold. Each data point was taken after at least one hour of unchanging reactor effluent composition.

4.4 CATALYST SCREENING TEST RESULTS

The data from the screening tests has been organized into six groups. Data summaries and evaluation for each group are presented in separate subsections.

Catalysts considered as meriting further investigation were subjected to parametric and SO_2 effect studies; data from these studies are presented in Section 4.5. The criteria used for labeling a catalyst as a promising candidate for power plant utilization, therefore meriting further investigation, varied somewhat with the process in which the activity was exhibited and with the products of the reaction. In general, at least 50% NO conversion was required as a minimum under the nominal screening test conditions (Section 4.3). For NO decomposition somewhat lower conversions were considered acceptable for further testing. NO oxidation conversions as low as 10-20% were also considered acceptable because the screening test temperature was relatively high for this reaction (the decomposition and oxidation tests were performed simultaneously, therefore, a compromise temperature was used).

4.4.1 Platinum and Platinum-Molybdenum Catalysts

Table 22 summarizes the catalyst screening test data taken with SO_2-free synthetic flue gas on alumina supported Pt (NA-1) and Pt-Mo (NA-3 and NA-4) catalysts. The NA-1 sample was a commercial catalyst prepared by Engelhard. The NA-3 and NA-4 samples were prepared at TRW on a commercial support (Section 3.2). The NA-3 catalyst was in the form of 1.6 mm (1/16 inch) spheres; the other two catalysts in this table and those in the subsequent tables of this section were 3.2 x 3.2 mm (1/8 x 1/8 inch) cylinders. The NA-4 sample was prepared from NA-3 by reshaping it into the cylinder form.

Data from Test No. 1, the decomposition and oxidation screening test, indicates that both the Pt and the Pt-Mo catalysts exhibited potential in NO decomposition but no activity toward NO oxidation. However, when the nominal 3% oxygen concentration in the synthetic flue gas was reduced to 0.5%, the NO decomposition activity of Pt was severely reduced. Similar oxygen effect was observed during the selective NO reduction tests with H_2 (compare NO conversions in Test Nos. 3 and 4) and with CO (Test Nos. 6 and 7). Since

Table 22. CATALYST SCREENING TEST RESULTS (Pt AND Pt-Mo CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents in Reactor Effluent [b]					NO Reduct. or Decomp. (%)	NO Oxida-tion (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-1 (0.5% Pt on alumina)	1	3	1023	0	0	0	561	0	0	-	-	45.2	0	-
	1	0.5	1077	0	0	0	926	0	N.A.	-	-	14.0	0	-
	2	3	1061	707	0	0	724	0	150	-	0	31.8	0	215[f]
	3	3	1063	0	1030	0	568	0	0	-	0	46.6	0	-
	4	0.5	1059	0	1048	0	854	0	0	-	0	19.4	0	-
	5	0.5	1022	0	11000	0	14	0	0	-	515	98.6	0	-
	6	3	1081	0	0	995	523	0	0	29	-	46.0	0	-
	7	0.5	1050	0	0	995	813	0	0	0	-	22.6	0	-
	8	0.5	1036	0	0	10355	0	0	0	0	-	100	0	-
NA-3 (22.2% Mo 0.1% Pt on alumina)	1	3	1008	0	0	0	778	0	0	-	-	22.8	0	-
	2	3	1065	768	0	0	660	0	290	-	0	38.0	0	184[f]
	2[c]	3	968	760	0	0	328	0	340	-	0	66.1	0	76[f]
	2[d]	3	968	760	0	0	346	0	385	-	N.A.	64.3	0	83[f]
	2[e]	3	968	760	0	0	400	0	356	-	N.A.	58.7	0	100[f]
	3	3	1098	0	1030	0	803	0	0	-	0	26.9	0	-
	4	0.5	1047	0	1030	0	918	0	0	-	0	12.3	0	-
	5	0.5	1064	0	11000	0	0	0	0	-	548	100.0	0	-
	6	3	1040	0	0	1048	780	0	0	0	0	25.0	0	-
	7	0.5	1020	0	0	1073	868	0	0	0	0	14.9	0	-
	8	0.5	1026	0	0	11000	0	0	0	200	0	100.0	0	-
NA-4 (Pel-letized NA-3)	1	3	898	6	0	0	675	0	0	-	-	24.8	0	-
	2	3	931	793	0	0	502	0	318	-	0	46.1	0	177[f]
	3	3	932	0	1012	0	670	0	0	-	0	28.1	0	-
	4	0.5	988	0	1012	0	801	0	0	-	0	18.9	0	-
	5	0.5	988	0	11000	0	185	0	0	-	545	81.3	0	-
	6	3	879	0	0	1003	608	0	0	0	0	30.8	0	-
	7	0.5	937	0	0	1003	854	0	0	0	0	14.3	0	-
	7[g]	0.5	1007	0	0	1030	886	0	0	0	0	12.0	0	-
	8	0.5	1059	0	0	11000	114	0	0	700	230	89.2	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

[c] 14,000 hr^{-1} space velocity (nominal 20,000 hr^{-1})

[d] Reaction temperature 263°C (nominal 400°C)

[e] Reaction temperature 300°C

[f] Calculated on the basis of the desired reaction $6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$.

[g] Repeat test after overnight air exposure at 400°C.

neither H_2 nor CO selectivity for NO reduction appears evident (NO conversions during Test Nos. 1, 3, and 6 are nearly identical), the oxygen effect observed during the selective tests must be also due to NO decomposition. The Pt-Mo catalysts (NA-3 and NA-4) exhibited the same behavior except that the extent of NO decomposition on these catalysts, under nominal flue gas O_2 concentration (3%), was lower than that obtained on Pt. Thus, the tentative conclusion was drawn that NO decomposition increases with increasing O_2 concentration in the range of 0.5 to 3%.

Comparison of data derived from Test Nos. 1, 3, and 6 for Pt and Pt-Mo catalysts reveals that the activity of platinum toward NO decomposition is twice that of the latter catalysts. However, this difference in activity was not verified; the NA-1 sample was accidentally discarded before any reproducibility tests on NO decomposition could be performed. Attempts to reproduce the 45.2% NO decomposition on a new batch of 0.5% Pt on alumina, acquired from Engelhard, failed. A reproducible value of about 27% NO decomposition was obtained with the new catalyst. This NO conversion value is closer to that generated on NA-3 and NA-4 catalysts. The 27% value was assumed to be more reliable even though the 45% decomposition attained in Test No. 1 of NA-1 was indirectly reproduced in Test Nos. 3 and 6 performed on the same sample.

The 27% NO decomposition value was considered sufficient to subject platinum to parametric investigation (Section 4.5).

As expected (Section 3.2) selective NO reduction by NH_3 on Pt at 400°C was inefficient (Test No. 2). The data on NA-1 indicates only 32% NO conversion; this value is lower than that obtained in Test No. 1 which implies that NH_3 inhibits NO decomposition on platinum. However, even if it is assumed that the true NO decomposition value is 27%, the use of Pt to promote the selective NO-NH_3 reaction at 400°C is not justified. Of course, Pt is a very efficient catalyst for the above reaction at lower temperatures, but only with SO_2-free flue gas. As is indicated in Section 4.5 (parametric investigations), SO_2-poisoned Pt catalysts at 200-300°C can be regenerated at 400°C by air. The implication of this finding is that if Pt were to provide the NO-NH_3 reduction reaction at 400°C its use with SO_2 flue gases would have been possible.

The objective of screening the NA-3 and NA-4 catalysts was to investigate the effect of Mo on Pt activity (especially its activity for the NO-NH_3 reaction). The data in Table 22 indicates that the Pt promoted Mo catalysts behaved very similar to the supported Pt catalyst (NA-1). NO reduction by ammonia was low at 400°C, but increased with decreasing temperature. Also, both catalyst types promoted the production of N_2O in quantities nearly equal to NO reduced (on per mole basis).* Thus, Pt activity does not appear to be materially affected by the large presence of Mo.

The last column in Table 22 indicates the percent excess usage of ammonia during Test No. 2. This excess value was calculated from the reactor "in" and "out" values of NO and NH_3 and on the basis of the reaction

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$$

According to their reaction, the quantity of ammonia consumed in Test No. 2 should equal 67% of the NO reduced (mole or volume basis); additional ammonia consumption is labeled "excess usage".

As expected, the Pt catalyst was a very efficient promoter of nonselective NO reduction with both H_2 and CO (Test Nos. 5 and 8). However, with H_2 as the reductant NH_3 production was higher than expected at 400°C under very nearly stoichiometric oxidant-reductant conditions. The Pt-Mo catalysts indicated activity equal to Pt for these reactions (the slightly lower activity exhibited by NA-4 must be due to surface area reduction during preparation).

In addition to generating baseline data on Test Nos. 1 through 8, the screening tests on Pt and Pt-Mo catalysts furnished the following information:

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* To our knowledge, N_2O production during the NO-NH_3 reduction reaction on Pt in the presence of O_2 had not been reported prior to being reported in this program's interim reports.

- Pt was identified as a potential NO decomposition catalyst meriting further investigation.

- The Pt-Mo catalysts behaved very similar to the Pt catalyst in the Table 22 experimental matrix. In view of the lower Pt content of these catalysts, they may be preferable to Pt because of cost considerations. However, the role of Mo must be established more precisely and longer-term activity tests must be performed prior to such substitution.

4.4.2 Molybdenum-Based Catalysts

Table 23 presents the screening test data generated on four molybdenum-on-alumina catalysts (NA-5 through 8) and one alumina supported molybdenum-cobalt oxide catalyst (NA-9). These catalysts were prepared by TRW and UCLA as described in Section 4.2; the first four differ from each other either in Mo content or in pretreatment prior to testing. In general, catalysts were not activated prior to testing (other than exposure to flue gas until steady state was reached), but NA-7 and NA-8 were reduced in H_2 prior to screen testing.

The first three catalysts of Table 23 were subjected to the entire screening test matrix; the last two were only tested for NO decomposition or oxidation potential (Test No. 1) and for activity in Test No. 2 (NO-NH_3 selective reduction). One of the catalysts (NA-7) was subjected to additional off-nominal temperature and space velocity testing in order to compare the derived data to that generated on the Pt-Mo catalysts (Table 22). The Mo catalysts were selected primarily for testing their potential in the selective reduction of NO with ammonia. Their selection was based on the activity they exhibited toward hydrazine decomposition (TRW patent).

The data in Table 23 verified the expectation that Mo catalysts would promote NO reduction by NH_3 in the presence of oxygen (Test No. 2 data). Under the screening test conditions (400°C, 20,000 hr^{-1}) about 46% NO reduction was achieved; on NA-6 NO reduction was 40% while on NA-9 (the Co-Mo oxide

Table 23. CATALYST SCREENING TEST RESULTS (Mo BASED CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents In Reactor Effluent[b]					NO Reduct. or Decomp. (%)	NO Oxida-tion (%)	Excess NH3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-5 (27% Mo on Al_2O_3)	1	3	996	0	0	0	968	0	0	-	-	2.8	0	-
	2	3	1045	752	0	0	560	0	0	-	250	46.4	0	55
	3	3	995	0	1020	0	969	0	0	-	0	2.6	0	-
	4	0.5	1031	0	1020	0	1006	0	0	-	0	2.4	0	-
	5	0.5	1047	0	11000	0	950	0	0	-	0	9.3	0	-
	6	3	1050	0	0	1003	1036	0	0	550	0	1.3	0	-
	7	0.5	1012	0	0	1003	1007	0	0	865	0	0.5	0	-
	8	0.5	1026	0	0	11000	1013	0	0	N.A.	0	1.3	0	-
NA-6 (14.7% Mo on Al_2O_3)	1	3	1036	-	-	-	1028	0	0	-	-	0.7	0	-
	2	3	977	628	-	-	589	0	0	-	358	39.7	0	143
	3	3	1055	-	1003	-	1040	0	0	-	0	1.4	0	-
	4	0.5	1020	-	1003	-	1015	0	0	-	0	0.5	0	-
	5	0.5	1020	-	11000	-	1007	0	0	-	15	1.4	0	-
	6	3	1007	-	-	1003	981	0	0	836	0	2.6	0	-
	7	0.5	986	-	-	1003	964	0	0	897	0	2.2	0	-
	8	0.5	993	-	-	11000	989	0	0	~11000	0	0.4	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

Table 23. (Continued) CATALYST SCREENING TEST RESULTS (Mo BASED CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition					Monitored Gas Constituents in Reactor Effluent					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-7 (14.7% Mo on Al_2O_3)[c]	1	3	1022	0	0	0	1005	0	0	-	-	1.7	0	-
	2	3	975	729	0	0	530	0	0	-	246	45.6	0	62
	2[d]	3	914	718	0	0	684	0	0	-	447	25.2	0	77
	2[e]	3	916	718	0	0	532	0	0	-	299	41.9	0	64
	2	3	931	740	0	0	501	0	0	-	242	46.2	0	74
	2[f]	3	931	740	0	0	522	0	90	-	192	43.9	0	100
	2[g]	3	931	740	0	0	540	0	66	-	144	42.0	0	129
	2[h]	3	932	740	0	0	744	0	0	-	515	20.2	0	80
	2	3	937	873	0	0	445	0	0	0	400	52.5	0	44
	2	3	916	1112	0	0	412	0	0	0	585	55.0	0	57
	2	3	937	866	0	0	441	0	0	0	381	53.0	0	47
	2[i]	3	933	1140	0	0	276	0	76	0	259	79.0	0	80
	3	3	1052	0	1038	0	1021	0	0	-	0	2.9	0	-
	4	0.5	1036	0	1038	0	1030	0	0	-	0	0.6	0	-
	5	0.5	1036	0	10355	0	955	0	0	-	0	7.8	0	-
	6	3	1048	0	0	1000	1029	0	0	1000	0	1.8	0	-
	7	0.5	1022	0	0	1012	1014	0	0	1000	0	0.8	0	-
	8	0.5	1023	0	0	10355	1014	0	0	9690	N.A.	0.9	0	-
NA-8 (14.7% Mo on Al_2O_3)[j]	1	3	910	0	0	0	905	0	0	0	0	0.6	0	-
	2	3	950	734	0	0	521	0	0	0	335	45.2	0	40
NA-9 (2.7% Co_3O_4 15% MoO_3)	1	3	1029	0	0	0	1023	0	0	0	0	0.6	0	[illegible]
	2	3	992	812	0	0	847	0	0	0	627	14.6	0	91

[c] Catalyst reduced for 20 hours at 480°C in H_2

[d] Reaction temperature 300°C

[e] Reaction temperature 350°C

[f] Reaction temperature 450°C

[g] Reaction temperature 500°C

[g] Reaction temperature 500°C

[h] Reaction temperature 275°C

[i] 10,000 hr^{-1} space velocity (STP) (all others at 20,00 hr^{-1})

[j] Catalyst reduced at 700°C for four hours in H_2

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catalyst) it was only 15%. The extent of NO reduction did not appear to be influenced either by the Mo content of the catalyst in the 14.7 to 27% range or by catalyst pretreatment (H_2 reduction). However, a slight improvement in activity was observed with exposure time to NH_3 containing flue gas (NA-7). The tests on NA-7 were performed in the presented sequence; the data from the last three runs of Test No. 2, performed under nominal conditions, indicate NO reduction in the 53-55% range versus 46% observed earlier.

Nitric oxide reduction improved dramatically with decreasing space velocity (79% NO reduction at 10,000 hr^{-1}, NA-7). Maximum NO reduction appeared to occur at 400 ± 50°C; at lower temperatures dropped off severely (only 20% at 275°C). This behavior is contrary to that exhibited by the Pt-Mo catalysts; it supports the conclusion drawn in the previous section that the Pt-Mo catalyst behaves more like Pt than Mo catalyst. The same conclusion is drawn from the fact that the Mo catalyst did not exhibit appreciable activity in Test Nos. 1, 5 and 8 (NO decomposition and nonselective reduction).

The Mo catalyst must be considered as a potential candidate for NO_x abatement by means of the selective NH_3 reduction process. They were not investigated further, however, because they were ranked third and only the top two ranked catalysts underwent parametric investigation. As indicated above, NA-7 was subjected to a temperature scan and two values of space velocity.

4.4.3 Rare-Earth-Based Catalysts

Table 24 presents the data derived from screening tests performed on seven rare earth and rare-earth-transition metal oxide mixtures (NA-10 through NA-16). NA-10 was a commercial rare-earth oxide mixture (refined ore); all the other catalysts in this group were prepared at UCLA (refer to Section 4.2 for method of preparation). These catalysts were screened primarily for NO oxidation-decomposition potential.

The data in Table 24 indicates that under the nominal screening test conditions these catalysts failed to promote any of the NO_x abatement reactions. The only exception was NA-15 (15% $GdVO_3$ on alumina) which appeared to promote

Table 24. CATALYST SCREENING TEST RESULTS (RARE EARTH OXIDE BASED CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents in Reactor Effluent[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-11 (Rare earth-cobalt oxides on alumina)	1	3	1022	0	0	0	1004	0	-	-	-	1.8	0	-
	1	3	1011	0	0	0	620	~150	0	-	-	23.8	14.8	-
	2	3	1011	735	0	0	654	0	0	-	325	35.3	0	72
	3	3	1011	0	1012	0	961	0	0	-	0	4.9	0	-
	4	0.5	1011	0	1012	0	974	0	0	-	0	3.7	0	-
	5	0.5	1011	0	11000	0	1038	0	0	-	0	0	0	-
	6	3	1011	0	0	1003	1018	0	0	318	0	0	0	-
	7	0.5	1011	0	0	1003	1020	0	0	737	0	0	0	-
	8	0.5	1011	0	0	11000	1007	0	0	3045	0	0	0	-
NA-12 (NA-11 + 10%Pb)	1	3	1012	0	0	0	658	~140	0	-	-	21.1	13.8	-
	2	3	1012	700	0	0	964	0	0	-	0	4.7	0	>800
	3	3	1012	0	1057	0	927	0	0	-	0	8.4	0	-
	4	0.5	1012	0	1067	0	913	0	0	-	0	9.9	0	-
	5	0.5	1012	0	11000	0	1029	0	0	-	0	0	0	-
	6	3	1012	0	0	1012	879	0	0	60	0	13.1	0	-
	7	0.5	1012	0	0	1012	973	0	0	75	0	3.9	0	-
	8	0.5	1012	0	0	10355	913	0	0	2500	0	9.9	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

Table 24. (CONTINUED) CATALYST SCREENING TEST RESULTS (RARE EARTH OXIDE BASED CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents in Reactor Effluent[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-13 (15% $Gd_2(MoO_4)_3$ on Al_2O_3)	1	3	1014	0	0	0	1010	0	0	0	0	0.4	0	-
	2	3	997	792	0	0	937	0	0	0	730	6.0	0	55
	3	3	1021	0	978	0	1000	0	0	0	0	2.1	0	-
	4	0.5	1000	0	978	0	978	0	0	0	0	2.2	0	-
	5	0.5	936	0	9515	0	917	0	0	0	0	2.0	0	-
	6	3	993	0	0	962	960	0	0	962	0	3.3	0	-
	7	0.5	995	0	0	962	929	0	0	940	0	6.6	0	-
	8	0.5	950	0	0	9780	941	0	0	9620	0	0.9	0	-
NA-14 (15% $GdMoO_3$ on Al_2O_3)	1	3	954	0	0	0	947	0	0	0	0	0.7	0	-
	2	3	907	904	0	0	801	0	0	0	743	11.7	0	127
NA-15 (15% $GdVO_3$ on Al_2O_3)	1	3	1002	0	0	0	876	67	0	0	0	5.9	6.7	-
	2	3	1004	764	0	0	390	0	0	0	405	61.2	0	-14
	3	3	1009	0	978	0	876	52	0	0	0	8.0	5.2	-
	4	0.5	971	0	978	0	933	0	0	0	0	3.9	0	-
	5	0.5	955	0	10059	0	900	0	0	0	0	5.8	0	-
	6	3	1007	0	0	1030	902	0	0	986	0	10.4	0	-
	7	0.5	972	0	0	1030	957	0	0	986	0	1.5	0	-
	8	0.5	869	0	0	9780	841	0	0	N.A.	0	3.2	0	-
NA-16 (15% $LaCoO_3$ on Al_2O_3)	1	3	1017	0	0	0	912	0	0	0	0	10.3	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

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NO oxidation (Test No. 1). The produced NO_2 corresponded to less than 10% NO oxidation, but at 400°C this extent of conversion may be significant. The same catalyst promoted the selective reduction of NO with NH_3, but to no greater extent than vanadia on alumina alone did. These catalysts were nct investigated further.

4.4.4 Copper Oxide and Lead Doped Copper Oxide Catalysts

The catalysts in this group were prepared by UCLA. The group includes one copper oxide on alumina catalyst (16.5% CUO, 83.5% alumina), NA-17, and three lead-doped CuO catalysts (1%, 5%, and 10% lead) prepared from NA-17. These catalysts were selected for screening as potential promoters for the selective reduction of NO by NH_3 and CO. As indicated in Section 3.2, CuO has been suggested as a promising Test No. 2 catalyst (selective NO-NH_3 reaction), but convincing data was not available. Earlier experimental work at UCLA had suggested that lead doped CuO may prove to be an active catalyst for the selective reduction of NO with CO by inhibiting the CO-O_2 reaction. The latter expectation did not materialize, but copper oxide did exhibit some activity for the selective reduction of NO with NH_3. The activity of the lead doped CuO in the NO-NH_3 reaction was significant. The latter catalysts indicated higher activity than CuO in the nonselective NO reduction with H_2, also. Table 25 presents the screening test data generated on this group of catalysts.

The data indicates that lead improves the activity of CuO in virtually all the reactions included in the catalyst screening test matrix. Significant NO reduction was obtained in Test Nos. 2 and 5 (selective reduction with NH_3 and nonselective reduction with H_2). In Test No. 2 performance, the lead doped CuO could be ranked equal to the Mo catalysts; toxicity considerations, however, should rank the Mo catalysts higher. The NO conversions in Test No. 5, even though appreciable, do not justify the use of these catalysts in nonselective NO_x abatement by reduction, but they may be good candidates for simultaneous NO_x-SO_x abatement by this process especially if they do not promote H_2S production.

Table 25. CATALYST SCREENING TEST RESULTS (COPPER AND COPPER-LEAD CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents In Reactor Effluent[b]					NO Reduct. or Decomp. (%)	NO Oxida-tion (%)	Excess NH3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-17 (16.5% CuO on alumina)	1	3	946	0	0	0	931	0	0	-	-	1.6	0	-
	2	3	946	557	0	0	594	0	0	-	125	37.2	0	84?
	2[c]	3	1021	750	0	0	776	0	0	-	533	24.0	0	33
	3	3	1029	0	1049	0	923	0	0	-	120	10.3	0	-
	4	0.5	1029	0	1049	0	951	0	0	-	33	7.6	0	-
	5	0.5	1029	0	11700	0	871	0	0	-	14	15.4	0	-
	6	3	1029	0	0	1021	1027	0	0	548	0	0	0	-
	7	0.5	1029	0	0	1021	988	0	0	5[illegible]4	0	4.0	0	-
	8	0.5	1029	0	0	11000	990	0	0	6118	0	3.8	0	-
NA-18 (NA-17 + 1% Pb)	1	3	1019	0	0	0	889	0	0	-	0	12.8	0	-
	2	3	1019	723	0	0	489	0	38	-	254	52.0	0	20
	3	3	1019	0	1048	0	940	0	0	-	0	7.8	0	-
	4	0.5	1019	0	1067	0	962	0	0	-	0	5.6	0	-
	5	0.5	1019	0	11000	0	767	0	0	-	0	24.7	0	-
	6	3	1030	0	0	1057	917	0	0	602	0	11.0	0	-
	7	0.5	1030	0	0	1020	933	0	0	530	0	9.4	0	-
	8	0.5	1030	0	0	11000	936	0	0	5398	0	9.1	0	-
NA-19 (NA-17 + 5% Pb)	1	3	1020	0	0	0	968	0	0	-	-	5.1	0	-
	2	3	1020	761	0	0	472	0	63	-	219	53.7	0	26
	3	3	1020	0	1029	0	983	0	0	-	0	3.6	0	-
	4	0.5	1020	0	1067	0	992	0	0	-	15	2.7	0	-
	5	0.5	1020	0	10355	0	815	0	0	-	0	20.1	0	-
	6	3	1020	0	0	1067	1015	0	0	370	0	0.4	0	-
	7	0.5	1020	0	0	1067	994	0	0	407	0	2.5	0	-
	8	0.5	1020	0	0	11000	854	0	0	4680	0	16.3	0	-
NA-20 (NA-17 + 10% Pb)	1	3	1048	0	0	0	955	0	0	-	-	8.9	0	-
	2	3	1048	651	0	0	504	0	0	-	274	51.9	0	4
	3	3	1048	0	1030	0	1020	0	0	-	26	2.7	0	-
	4	0.5	1048	0	1030	0	1002	0	0	-	0	4.8	0	-
	5	0.5	1048	0	11000	0	663	0	0	-	0	36.7	0	-
	6	3	1048	0	0	1030	1024	0	0	316	0	2.3	0	-
	7	0.5	1048	0	0	1030	1017	0	0	318	0	3.0	0	-
	8	0.5	1048	0	0	11000	783	0	0	3108	0	25.3	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

[c] Catalyst temperature was 250°C for this test; all other tests were performed at 400°C.

These catalysts were not investigated further again because of ranking and not because of lack of potential.

4.4.5 Tungsten Oxide and Vanadia Catalyst

Several investigators have proposed the use of these catalysts for NO_x abatement by selective reduction with ammonia (Table 12, Section 3.2). Insufficient data on claims made on these catalysts led to the decision to screen under this program the catalysts presented in Table 26. The NA-21 and NA-22 tungsten oxide catalyst were prepared by TRW; they represent the same catalyst in two shapes. As it was the case with the Mo catalysts, NA-21 and NA-22 were active in hydrazine decomposition. The other three catalysts in Table 4.9 represent commercial preparations (one tungsten oxide and two vanadia catalysts). Only one tungsten oxide (NA-22) and one vanadia catalyst (NA-24) were subjected to the entire test matrix. The other three catalysts, which were similar to or were derived from the first two, were only subjected to tests where potential activity had been indicated earlier.

The data in Table 26 indicates that regardless of claims, the WO_3 catalysts did not appreciably promote the selective reduction of NO by NH_3 under screening test conditions; this is at least true for the catalyst preparations tested under this program. Some activity was exhibited toward NO decomposition and nonselective NO reduction with H_2, but not sufficient to suggest additional investigation under this program.

The vanadia catalysts (NA-24 and NA-25) promoted substantial NO reduction under Test No. 2 conditions. These catalysts were selected for parametric and SO_2 effect investigations; the generated data is presented in the next section. It should be noted that the vanadia catalysts did not promote N_2O production and that the excess ammonia consumption was negligible.

4.4.6 Iron and Chromium Based Catalysts

In Section 3 of this report it was indicated that iron, chromium, and iron-chromium catalysts, especially the oxides, have been investigated and to a lesser extent suggested for NO_x abatement utilization. Predominantly,

Table 26. CATALYST SCREENING TEST RESULTS (TUNGSTEN OXIDE AND VANADIA CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Gas Constituents in Reactor Effluent[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-21 (13.1% W on alumina) 20-30 mesh	1	3	1034	0	0	0	911	0	0	-	-	11.9	0	-
	3	3	1034	0	1030	0	894	0	N.A.	-	N.A.	13.5	0	-
	4	0.5	960	0	1030	0	746	0	0	-	N.A.	22.3	0	-
NA-22 (13.1% W on alumina) 1/8 inch cylinders	1	3	1029	0	0	0	895	0	0	-	-	13.0	0	-
	2	3	1042	768	0	0	876	0	180	-	422	16.0	0	786
	3	3	1033	0	978	0	987	0	0	-	0	4.8	0	-
	4	0.5	1064	0	1003	0	1046	0	0	-	0	1.7	0	-
	5	0.5	1053	0	10669	0	658	0	0	-	217	37.5	0	-
	6	3	1038	0	0	1003	996	0	0	475	0	4.0	0	-
	7	0.5	1057	0	0	1003	1034	0	0	793	0	2.2	0	-
	8	0.5	1061	0	0	11000	952	0	0	10355	0	10.3	0	-
NA-23 (10% WO_3 on Al_2O_3) Harshaw	1	3	1014	0	0	0	1009	0	0	0	0	0.5	0	-
	2	3	1023	942	0	0	959	0	0	0	845	6.2	0	127
	3	3	1037	0	1000	0	1004	0	0	0	0	3.2	0	-
	4	0.5	1119	0	1000	0	1024	0	0	0	0	0	0	-
	5	0.5	1010	0	11000	0	1004	0	0	0	0	0.6	0	-
NA-24 (10% V_2O_5 on Al_2O_3) Filtrol	1	3	953	0	0	0	895	0	0	-	-	6.1	0	-
	2	3	946	751	0	0	318	0	72	-	215	66.4	0	28
	3	3	969	0	978	0	936	0	0	-	0	3.4	0	-
	4	0.5	1050	0	978	0	1038	0	0	-	0	1.1	0	-
	5	0.5	1048	0	10670	0	841	0	0	-	0	19.8	0	-
	6	3	1031	0	0	946	975	0	0	760	0	3.8	0	-
	7	0.5	966	0	0	978	974	0	0	826	0	0	0	-
	8	0.5	1014	0	0	11000	976	0	0	11000	0	3.7	0	-
NA-25 (10% V_2O_5 on Al_2O_3) Harshaw	2	3	969	670	0	0	352	0	0	0	75	63.7	0	45

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

their use has been proposed for selective NO_x reduction with NH_3 and for nonselective NO_x reduction with CO. It was, therefore, decided to screen several of them under the conditions of the screening test matrix.

Table 27 presents the data derived from five mixed iron-chromium oxide catalysts and one chromium oxide catalyst. The first two Fe-Cr oxide mixtures (NA-26 and NA-27) were commercial preparations containing magnesia and silica in addition to the iron and chromium oxides (Girdler catalysts). The other three mixed oxide catalysts were prepared at UCLA and were composed of iron and chromium oxides supported on alumina. The chromium oxide on alumina catalyst was also prepared at UCLA.

The data in Table 27 shows that activity of any significance was exhibited only during Test No. 2 by this group of catalysts. It is also evident from the data that catalyst composition and possibly catalyst preparation play a substantial role in the activity of these catalysts. The catalysts with high iron oxide content (NA-26, 27 and 30) exhibited low activity in Test No. 2 compared to that shown by NA-28 and NA-29. The 15% chromia on alumina catalyst showed moderate activity during the same test (selective $NO-NH_3$ reduction). The two UCLA-prepared, low active metal content catalysts (NA-28 and NA-29) exhibited the same activity as the vanadia catalysts for the selective reduction of NO by NH_3 in the presence of 3% oxygen; thus, they were also selected for parametric and SO_2 effect studies (Section 4.5). It should be noted that N_2O was not produced on these catalysts and that excess NH_3 utilization was negligible.

Table 28 presents the data from the last group of catalysts screened under this program. They are three iron oxides on alumina and two iron on graphite catalysts. The latter two catalysts were investigated because of reported activity in ammonia synthesis. The iron oxides on alumina were screened in order to compare data derived from them to that generated on the chromia catalyst (NA-31) and on the mixed Fe-Cr oxide catalysts (NA-28 and NA-29).

The iron oxide catalysts exhibited lower activity than the mixed Fe-Cr oxide catalysts under Test No. 2. conditions. As indicated above, the chromia on

Table 27. CATALYST SCREENING TEST RESULTS (IRON-CHROMIUM OXIDE CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Outlet Gas Composition[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-26 (Girdler G3A) 80% Fe_2O_3, 7% Cr_2O_3, balance MgO, SiO_2 and graphite	1	3	1029	0	0	0	953	0	0	-	-	7.4	0	-
	2	3	1029	683	0	0	850	0	400	-	95	17.4	0	394
	3	3	1029	0	1029	0	980	0	0	-	0	4.8	0	-
	4	0.5	1029	0	1048	0	998	0	0	-	0	3.0	0	-
	5	0.5	1029	0	11000	0	958	0	0	-	0	6.9	0	-
	6	3	1029	0	0	1030	1031	0	0	654	0	0	0	-
	7	0.5	1029	0	0	1030	1018	0	0	697	0	1.0	0	-
	8	0.5	1029	0	0	11000	991	0	0	5400	0	3.7	0	-
NA-27 (Girdler Fe-Cr similar to NA-26)	2	3	1004	693	0	0	977	0	334	0	86	2.7	0	3270

Table 27. (Continued) CATALYST SCREENING TEST RESULTS (IRON-CHROMIUM OXIDE CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Outlet Gas Composition[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-28 (10% $Fe_2O_3 \cdot Cr_2O_3$ on Al_2O_3	1	3	960	0	0	0	874	0	0	0	0	8.9	0	-
	2	3	940	767	0	0	309	0	0	0	79	67.1	0	63
	3	3	947	0	954	0	909	0	0	0	0	4.0	0	-
	4	0.5	936	0	954	0	911	0	0	0	0	2.7	0	-
	5	0.5	935	0	10355	0	867	0	0	0	0	7.3	0	-
	6	3	960	0	0	995	924	0	0	898	0	3.8	0	-
	7	0.5	960	0	0	995	941	0	0	888	0	2.0	0	-
	8	0.5	992	0	0	10059	977	0	0	8835	0	1.5	0	-
NA-29 (NA-28 prepared from different salts)	1	3	931	0	0	0	863	0	0	0	0	7.3	0	-
	2	3	954	780	0	0	366	0	0	0	461	61.6	0	-18
	3	3	1016	0	1030	0	986	0	0	0	0	3.0	0	-
	4	0.5	996	0	1030	0	979	0	0	0	0	1.7	0	-
	5	0.5	985	0	10340	0	886	0	0	0	0	1.0	0	-
	6	3	1026	0	0	995	984	0	0	774	0	4.1	0	-
	7	0.5	1002	0	0	995	988	0	0	811	0	1.4	0	-
	8	0.5	1002	0	0	10340	964	0	0	10025	0	3.8	0	-

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Table 27. (Continued) CATALYST SCREENING TEST RESULTS (IRON-CHROMIUM OXIDE CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Outlet Gas Composition[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	H_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-30 (56.7% Fe_2O_3, 6.7% Cr_2O_3, 1.4% Al_2O_3 Pressed	1	3	958	0	0	0	885	0	0	0	0	7.6	0	-
	2	3	1022	800	0	0	693	0	105	0	296	32.2	0	130
	3	3	1018	0	978	0	960	0	0	0	0	5.7	0	-
	4	0.5	998	0	978	0	979	0	0	0	0	1.9	0	-
	5	0.5	1007	0	10059	0	969	0	0	0	0	3.8	0	-
	6	3	1064	0	0	0	1017	0	0	978	0	4.4	0	-
	7	0.5	1015	0	0	0	1004	0	0	978	0	1.1	0	-
	8	0.5	1015	0	0	0	997	0	0	10059	0	4.8	0	-
CHROMIUM OXIDE CATALYST														
NA-31 (15% Cr_2O_3 on Al_2O_3) Pressed	2	3	1018	598	0	0	642	0	106	0	113	36.9	0	93

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

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Table 28. CATALYST SCREENING TEST RESULTS (IRON OXIDE AND IRON GRAPHITE CATALYSTS)

Catalyst No. and Type	Test No.	Feed Gas Composition[a]					Monitored Outlet Gas Composition[b]					NO Reduct. or Decomp. (%)	NO Oxidation (%)	Excess NH_3 Usage (%)
		O_2 (%)	NO (ppm)	NH_3 (ppm)	H_2 (ppm)	CO (ppm)	NO (ppm)	NO_2 (ppm)	N_2O (ppm)	CO (ppm)	NH_3 (ppm)			
NA-32 (15% Fe_2O_3 on Al_2O_3) pressed	2	3	1015	675	0	0	551	0	0	0	309	45.7	0	18
NA-33 (15% Fe_2O_3 on Al_2O_3) impregnated	1	3	1046	0	0	0	993	53	0	0	0	0	5.1	-
	2	3	988	756	0	0	502	0	0	0	275	49.2	0	48
	2	3	1007	940	0	0	480	0	0	0	595	52.3	0	-2
NA-34 (20% Fe_2O_3 on Al_2O_3) Harshaw	1	3	1018	0	0	0	1011	0	0	0	0	0.7	0	-
	2	3	975	852	0	0	822	0	0	0	753	15.7	0	-3
NA-35 (Iron on graphite)	1	3	1003	0	0	0	1013	0	0	-	-	0	0	-
	1[c]	3	1091	0	0	0	1103	0	0	-	-	0	0	-
	2	3	975	698	0	0	890	0	0	-	66?	12.0	0	632?
	2[c]	3	1041	1040	0	0	1010	0	0	-	771	3.0	0	269
	2[c]	3	1037	852	0	0	1034	0	0	-	826	0.3	0	26
	3	3	1036	0	978	0	1023	0	0	-	0	1.2	0	-
	4	0.5	997	0	1067	0	817	0	0	-	79	18.0	0	-
	5	0.5	989	0	11000	0	852	0	0	-	N.A.	13.9	0	-
	6	3	1036	0	0	995	1037	0	0	825	-	0	0	-
	7	0.5	1006	0	0	1030	1031	0	0	980	-	0	0	-
	8	0.5	997	0	0	10355	963	0	0	10250	-	3.3	0	-
NA-35 (Iron on graphite)	1	3	1015	0	0	0	990	0	0	-	-	2.5	0	-
	2	3	1015	748	0	0	956	0	0	-	73	5.8	0	0
	3	3	1034	0	962	0	1027	0	0	-	0	0.7	0	-
	4	0.5	988	0	962	0	988	0	0	-	0	0	0	-
	5	0.5	1021	0	11000	0	901	0	0	-	30	11.8	0	-
	6	3	1051	0	0	997	1041	0	0	423	-	1.0	0	-
	7	0.5	1007	0	0	997	966	0	0	793	-	1.1	0	-
	8	0.5	1015	0	0	11220	872	0	0	9662	-	14.1	0	-

[a] In addition to the indicated gas components the synthetic flue gas contained 14% CO_2 and 5% water vapor with the balance being nitrogen.

[b] Effluent hydrogen was not monitored.

[c] 14,000 hr^{-1} (STP) space velocity (nominal 20,000 hr^{-1})

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alumina catalyst had also shown lower activity than the mixed oxides for the same reaction. The tentative conclusion appears to be that a synergistic effect takes place when the two oxides are mixed. However, additional data is required on the effect of catalyst composition on its activity before the above conclusion becomes unequivocal. The exhibited activity by chromia and by the iron oxide catalysts toward the selective NO reduction by NH_3 must be considered promising. These catalysts were not investigated further.

The iron on graphite catalysts were in all respects inferior to the other iron based catalysts investigated in this program. The small activity toward the selective reduction of NO with H_2 (Test No. 4) exhibited by NA-35 does not appear real in view of the data generated under Test No. 6 (non-selective reduction).

4.5 PARAMETRIC INVESTIGATIONS ON PLATINUM, VANADIA, AND IRON-CHROMIUM OXIDE CATALYSTS

Several catalysts emerged from the screening tests (400°C, 20,000 hr^{-1}) as potentially useful in NO_x abatement in power plants and, therefore, meriting additional investigation. They were as follows:

- NO decomposition: Pt on alumina; Pt-Mo on alumina, and possibly WO_3.
- NO oxidation: possibly $GdVO_3$ on alumina.
- Selective NO reduction
  - (a) With NH_3: Pt (250°C), V_2O_5, $GdVO_3$, and $Fe_2O_3 \cdot Cr_2O_3$ on alumina (high activity); Pt-Mo, Mo, lead promoted CuO, Fe_2O_3 on alumina (substantial activity; rare earth-cobalt oxide, CuO, and Cr_2O_3 on alumina (medium activity).
  - (b) With H_2 or CO: none.

- Nonselective NO reduction with H_2 and CO: high activity Pt and Pt-Mo on alumina; several catalysts exhibited low to medium activity for the H_2-NO reaction.

Program schedule and budget considerations necessitated the selection of only three of the above catalysts for parametric and SO_2 effect investigation. These were Pt, V_2O_5, and $Fe_2O_3 \cdot Cr_2O_3$.

Platinum was selected principally for NO decomposition studies and for the SO_2 effect on its activity toward the NO-NH_3 reaction. However, some parametric investigations were performed on the NH_3-NO reaction on Pt in order to generate baseline data on this process and to probe N_2O production.

The vanadia on alumina catalyst was selected for its high activity in the promotion of the NO-NH_3 reaction in the presence of oxygen.

The iron-chromium oxide mixture catalyst was selected for the same reactions as the vanadia catalyst.

4.5.1 Platinum Catalysts

As indicated earlier, 45 and 27% NO decomposition was obtained on two batches of presumably identical composition 0.5% Pt on alumina Engelhard catalyst (NA-1 and NA-2) when an SO_2-free synthetic power plant flue gas was passed over the catalyst at 400°C and 20,000 hr^{-1} (STP) space velocity. Even though the two NO conversion values differ substantially, both values were considered as indicating promise for use in NO_x abatement by the most desirable method (decomposition). Thus, the NO decomposition reaction on Pt was investigated at several temperatures and at two space velocities. The generated data are presented in Table 29 and Figure 20. The following tentative conclusions can be drawn from these data:

- Decomposition of NO as a function of temperature goes through a maximum at or near 300°C.

Table 29. DECOMPOSITION OF NO ON Pt CATALYST (NA-2)

Inlet Gas Composition[a] NO (ppm)	Inlet Gas Composition[a] O_2 (%)	Space Velocity (hr^{-1} STP)	Temperature (°C)	Outlet Gas Composition NO (ppm)	Outlet Gas Composition N_2O (ppm)	Decomposition of NO (%)
1003	3	10,000	400	620	138	38.2
1023	3	10,000	400	635	33	37.9
1023	3	10,000	350	553	0	49.5
1091	3	10,000	300	518	0	52.5
1091	3	10,000	250	636	0	41.7
1091	3	10,000	308	520	0	52.3
1089	3	20,000	305	608	0	44.2
1089	3	20,000	350	708	0	35.0
1107	3	20,000	400	817	0	26.2
1000	3	20,000	255	646	0	35.4
1000	3	20,000	304	584	0	41.6
1054	3	20,000	356	667	0	36.7
1080	3	20,000	400	783	0	27.5

[a] Feed also contained 14% CO_2 and 5% H_2O in nitrogen.

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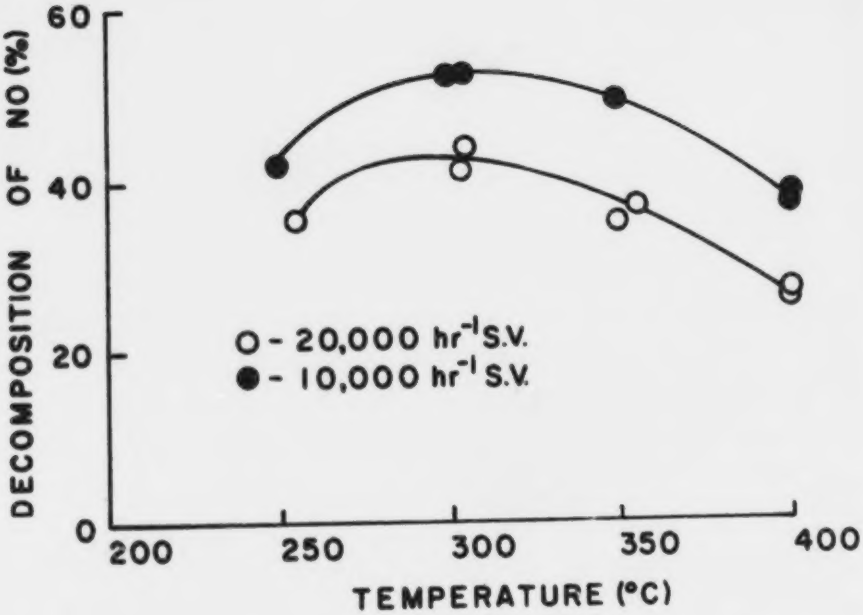

Figure 20. Decomposition of NO on Pt Catalyst (NA-2)

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- NO decomposition increases with decreasing space velocity in the range of 10,000 to 20,000 hr^{-1} (STP).

- NO decomposition decreases with decreasing oxygen concentration in the flue gas in the range of 0.5 to 3% oxygen (single point data, Table 22).

- The highest NO decomposition, 52.5%, was attained at 300°C and 10,000 hr^{-1} (STP).

The data appears to warrant the conclusion that Pt on alumina has exhibited sufficient NO decomposition potential to be seriously considered for power plant utilization, especially when complete NO_x abatement is not needed It should, however, be pointed out that this conclusion is based on small scale, short time testing; thus, additional experimental work is needed. The SO_2 effect should also be examined, although indirect evidence from the SO_2 effect experiments on the NH_3-NO-Pt process indicates that this flue gas constituent may not be a problem above 300°C.

Table 30 presents the data generated from experiments probing the effects of temperature, NH_3/NO ratio, NO and SO_2 concentrations, and space velocity on the activity of platinum in the selective reduction of NO by NH_3. The tests were initiated on the NA-1 catalyst (Engelhard 0.5Pt on alumina), but were switched to the NA-2 sample (same composition) when NA-1 was accidentally lost. Two samples of the latter catalyst were used. The data is presented in the sequence generated.

The data generated on the NA-1 catalyst at 250°C indicate that an immediate drop (approximately 15%) in catalytic activity occurs when 1000 ppm SO_2 is introduced to a flue gas containing near stochiometric quantities of ammonia (870 ppm) with respect to NO present. Increase of the NH_3-to-NO ratio (1110 ppm NH_3) restored the catalytic activity. The data appear to suggest that the observed decrease in NO reduction in Run 2 was due to NH_3 depletion

Table 30. PARAMETRIC EFFECTS ON PLATINUM CATALYSTS USED IN THE SELECTIVE REDUCTION OF NO BY NH_3

Run	Temp. (°C)	Inlet Gas Composition[a]			Outlet Gas Composition				NH_3/NO Inlet Ratio	Conv. of NO (%)	Space Velocity ($hr^{-1} \times 10^{-3}$)	SO_2 Exposure Time, Hours
		NO (ppm)	NH_3 (ppm)	SO_2 (ppm)	NO (ppm)	N_2O (ppm)	NH_3 (ppm)	SO_2 (ppm)				
		NA-1 CATALYST										
1	250	1016	870	0	271	571	N.A.[b]	N.A.	0.86	73.3	20	-
2	250	1062	870	1000	385	490	N.A.	N.A.	0.82	63.7	20	1
3	250	1055	1110	1000	280	670	N.A.	N.A.	1.05	73.5	20	2
4	250	1004	1110	0	256	670	N.A.	N.A.	1.11	74.5	20	-
		NA-2 CATALYST										
1	255	976	814	0	218	665	0	-	0.83	77.7	20	-
2	200	971	814	0	200	652	0	-	0.84	79.4	20	-
3	262	1047	846	0	290	625	0	-	0.81	73.2	20	-
4	300	1047	846	0	516	558	0	-	0.81	50.7	20	-
5	250	1046	846	0	358	765	0	-	0.81	65.8	20	-
6	212	1046	846	0	290	N.A.	0	-	0.81	72.2	20	-
7	209	993	799	0	238	689	0	-	0.80	76.0	20	-
8	209	1043	783	1000	663	278	345	80	0.75	36.4	20	1
9	209	1043	783	1000	804	318	389	320	0.75	22.9	20	2
10	260	1043	783	1000	537	415	108	450	0.75	48.5	20	3
11	300	1043	783	1000	516	458	N.A.	520	0.75	50.5	20	4
12	400	1043	783	1000	860	347	13	0	0.75	17.5	20	5
13	400	988	858	0	891	290	0	-	0.87	9.8	20	0
14	250	988	858	0	292	682	0	-	0.87	70.4	20	-
15	205	988	858	0	184	808	0	-	0.87	81.4	20	-
		NA-2 CATALYST										
1	250	1046	797	0	285	654	0	-	0.76	72.7	20	-
2	250	1046	754	0	456	389	0	-	0.55	56.4	20	-
3	250	1046	978	0	278	803	0	-	0.93	73.4	20	-
4	250	1054	1302	0	202	912	0	-	1.24	80.8	20	-
5	205	1054	1302	0	86	1405	0	-	1.24	91.8	20	-
6	205	1045	773	0	304	734	0	-	0.74	70.9	20	-
7	257	1051	771	0	304	591	0	-	0.73	71.0	20	-
8	205	1051	771	0	230	700	0	-	0.73	78.0	20	-
9	203	1051	1027	0	87	872	0	-	0.98	91.7	20	-
10	247	1051	1027	0	205	672	0	-	0.98	80.5	20	-
11	247	1051	1128	0	176	717	0	-	1.07	83.3	20	-
12	250	449	491	0	87	187	0	-	1.09	80.6	20	-
13	250	449	575	0	79	266	0	-	1.28	82.4	20	-
14	250	1058	1094	0	129	736	0	-	1.03	87.8	10	-
15	250	1003	1232	0	119	787	0	-	1.23	88.1	10	-

[a] Inlet gas also contained 5% H_2O and 14% CO_2 in N_2; 14 grams catalyst was used.

[b] NA = not available (data was not or could not be taken).

[c] Catalyst heated to 400°C for three hours prior to this test.

Table 30. (Continued) PARAMETRIC EFFECTS ON PLATINUM CATALYSTS USED IN THE SELECTIVE REDUCTION OF NO BY NH_3

Run	Temp. (°C)	Inlet Gas Composition[a]			Outlet Gas Composition				NH_3/NO Inlet Ratio	Conv. of NO (%)	Space Velocity ($Hr^{-1} \times 10^{-3}$)	SO_2 Exposure Time, Hours
		NO (ppm)	NH_3 (ppm)	SO_2 (ppm)	NO (ppm)	N_2O (ppm)	NH_3 (ppm)	SO_2 (ppm)				
16	250	1003	1232	1200	329	N.A.	N.A.	76	1.23	67.1	10	0.5
17	250	1003	1232	1200	296	N.A.	55	200	1.23	70.5	10	1.0
18	250	1083	1261	1200	296	N.A.	54	296	1.16	72.7	10	1.5
19	250	1064	1261	1200	633	N.A.	600	N.A.	1.19	40.5	10	19.5
20	250	1064	1261	0	198	N.A.	N.A.	-	1.19	81.4	10	-
21	250	1064	1261	0	105	N.A.	120	-	1.19	90.1	10	-
22	250	989	1189	0	124	787	86	-	1.20	87.5	10	-
23	250	989	1189	0	105	879	N.A.	-	1.20	89.4	10	-
24[c]	255	893	1250	0	116	796	0	-	1.39	87.0	10	-
25	255	961	1514	0	141	893	42	-	1.58	85.3	20	-
26	255	503	886	0	78	363	N.A.	-	1.76	84.4	20	-
27	255	259	304	0	57	131	0	-	1.17	77.9	20	-
28	255	259	520	0	29	195	0	-	2.01	88.8	20	-
29	255	259	600	0	29	N.A.	0	-	2.32	88.8	20	-
30	243	272	497	0	41	180	0	-	1.83	84.9	20	-
31	243	277	568	0	41	180	0	-	2.05	84.9	20	-
32	250	809	839	0	251	304	0	-	0.91	68.9	20	-
33	250	809	810	0	210	418	0	-	1.00	74.0	20	-
34	250	809	880	0	186	442	0	-	1.09	77.0	20	-
35	250	811	1230	0	131	508	0	-	1.52	83.8	20	-

[a] Inlet gas also contained 5% H_2O and 14% CO_2 in N_2; 14 grams catalyst was used.

[b] NA = not available (data was not or could not be taken).

[c] Catalyst heated to 400°C for three hours prior to this test.

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rather than loss of catalytic activity.* Thus, short time catalyst exposure to SO_2 at 250°C did not prove detrimental to its activity.

At 209°C the drop in NO conversion due to the presence of 1000 ppm SO_2 was also immediate and much more severe than at 250°C (NA-2, Sample A, Run 7 versus Run 8). NO conversion dropped from 76% to 36.4% after one hour exposure to SO_2 (Run 8) and to 22.9% after two hours (Run 9). Increasing the temperature to 400°C in three steps increased NO conversion until, at temperatures above 300°C, NH_3 oxidation by oxygen took over (Runs 10 through 12). Subsequent to removal of the SO_2 from the flue gas and temperature reduction to 250°C (Run 14) and to 205°C (Run 15) NO conversion was fully restored. In these experiments the NH_3 in the reactor effluent gas was measured. The data indicate that ammonia depletion was not the reason for the observed severe drop in NO conversion; it must have, therefore, been due to loss of catalytic activity which was fully restored by increasing the temperature to 400°C. The loss of catalytic activity for NO reduction may have been due to a competing reaction (e.g., SO_2 oxidation) or to physical blockage of catalyst active sites by a salt deposition on the catalyst. Evidence that either or both of these mechanisms of Pt poisoning could have occurred was furnished by the observed substantial SO_3 evolution during the temperature excursion to 400°C.

Longer-term SO_2 effect studies were performed on the second NA-2 sample (Sample B). In these experiments large excess of NH_3 and lower space velocity was used. As it was observed with NA-1, short-term (1.5 hours) catalyst exposure to SO_2 had no apparent effect on the activity of NA-2 at 250°C, provided excess NH_3 was present (Runs 16, 17, and 18); longer-term exposures, however, caused severe drop in activity (19.5 hours). Catalyst poisoning was again reversible (Run 20).

The above data clearly indicates that platinum is not recommended as a promoter for the NO-NH_3 selective reduction reaction if the flue gas to be

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[*] At the time, NH_3 determination in the effluent in the presence of SO_2 could not be made. Later, a specific ion electrode for NH_3 was acquired to perform these measurements.

treated contains SO_2 in quantities of 1000 ppm or more. The NO conversion dip because of SO_2 is immediate and severe in the temperature range where Pt is effective for NO reduction with NH_3; the required frequency of catalyst regeneration could be impractically high. It may be technically feasible to utilize Pt to promote the above reaction with flue gas containing only a few ppm SO_2 (1-10 ppm) because the frequency of regeneration would be lower. It should be noted, however, that a second catalytic reactor would be required which may render the process economically unfeasible. The true upper limit of SO_2 catalyst tolerance should be determined experimentally if economics and Pt availability permit the use of a second reactor. The planned tests at Environics (Dec. 1974) with 0.5% sulfur distillate oil (approx. 200 ppm SO_2 in the flue gas) should shed additional light on this subject.

Table 30 summarizes also the data generated by the variation of additional process parameters listed earlier (NH_3/NO, No concentration, temperature and space velocity). The following conclusions were drawn from these data:

- Temperature had a pronounced effect on NO reduction by NH_3 on Pt. Optimum conversion occurred in the 200-250°C range; NO conversion dropped off appreciably on both sides of this range (data obtained at temperatures below 200°C are not shown in Table 30).

- NO concentration in the range of 250 to 1000 ppm had little or no effect on NO conversion to N_2.

- The value of the NH_3-to-NO ratio had a pronounced effect on NO reduction in the range of 0.67 (stoichiometric value) to 1.2; at values higher than 1.2 the effect appeared to level off.

- Space velocity in the 5,000 to 20,000 hr^{-1} (STP) range had only a minor effect, if any, on NO reduction.

The NH_3-to-NO ratio, NO concentration, and space velocity effects are illustrated in Figure 21.

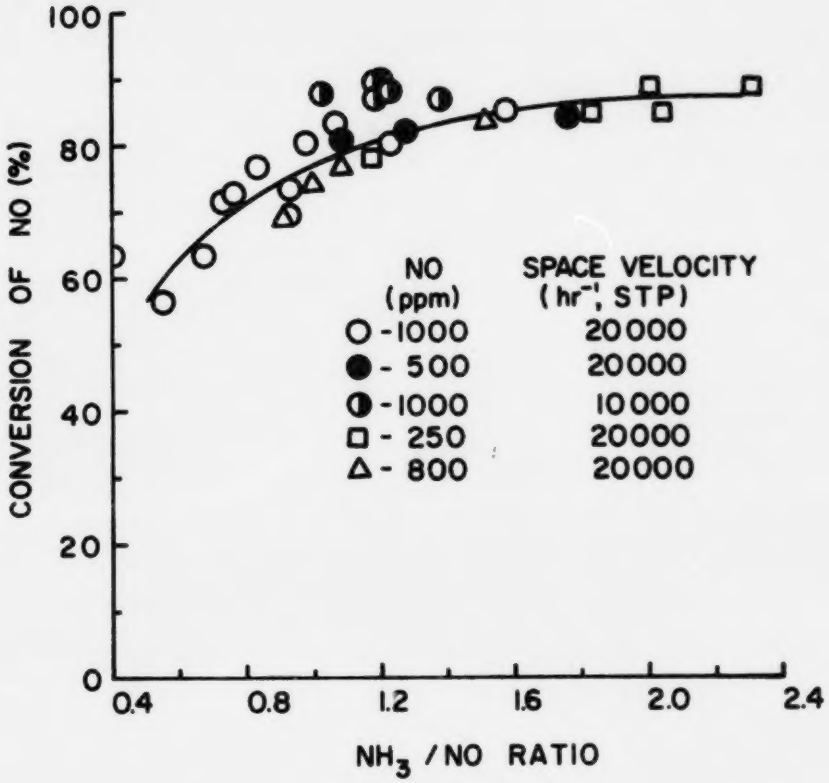

Figure 21. Reduction of NO with NH_3 on Pt catalyst at 250°C, (14% CO_2, 5% H_2O, 3% O_2 in N_2)

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It was indicated in the previous section that a substantial quantity of the NO reduced by NH_3 on Pt catalysts was apparently converted to N_2O instead of N_2. The parametric data verified N_2O production and under certain conditions indicated that the N_2O produced exceeded NO consumption. A number of experiments were performed to investigate N_2O production and the effect of oxygen on it. The generated data and inferences drawn from them are presented in Appendix A of this report. The important conclusion drawn from the data is that N_2O production on Pt can not be avoided as long as oxygen is present in the flue gas. In addition to oxygen, N_2O production was influenced by temperature and the NH_3-to-NO ratio.

4.5.2 Vanadia Catalysts

The catalyst screening tests (Section 4.4) revealed that both samples of commercial vanadia catalysts (NA-24, Filtrol and NA-25, Harshaw) appeared to be equivalent in activity for the selective reduction of NO with NH_3. Better than 60% NO conversion was attained on both catalysts at 400°C with no N_2O production and with insignificant excess NH_3 consumption. At 400°C these catalysts performed substantially better than Pt in the selective reduction of NO with NH_3. Thus, they were ranked top candidates, along with the Fe-Cr oxide catalysts, for further investigation.

Initially, both the Filtrol and Harshaw catalysts were subjected to parametric investigation, but inconsistencies in activity and physical instability eliminated the Filtrol catalyst from further testing. The Harshaw vanadia (NA-25) was subjected to temperature, oxygen and NO concentration, NH_3-to-NO ratio, space velocity, and SO_2 effect studies and proved a very promising candidate for utilization as a promoter of the NH_3-NO reaction in the presence of oxygen and SO_2.

Figure 22 presents data on the temperature and oxygen concentration effects generated with dry, CO_2-free flue gas on NA-25 at 20,000 hr^{-1} (STP). Water vapor and CO_2 were not used in these tests in order to separate the oxygen effect from that of H_2O and CO_2; the flue gas was also SO_2-free. The data in Figure 22 indicate that NO reduction increases with increasing oxygen

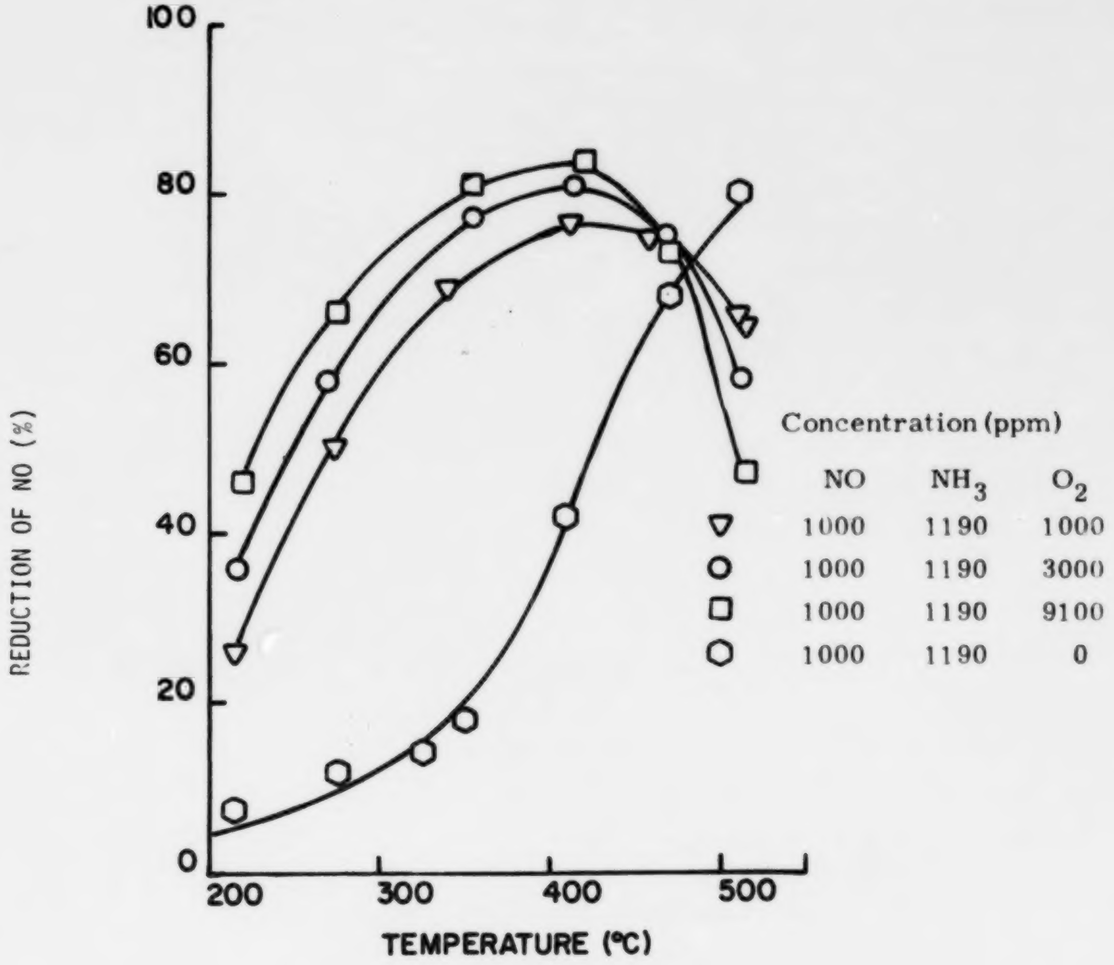

Figure 22. Effect of O_2 Concentration and Temperature on NO Reduction with NH_3 on V_2O_5 Catalyst (Harshaw).

concentration, but that this effect diminishes as the oxygen approaches typical flue gas oxygen concentration values and as the temperature reaches or exceeds the optimum reaction temperature. The data also indicates that the optimum temperature range for NO reduction by NH_3 on vanadia is 350-400°C.

The same optimum reaction temperature range was observed when the full flue gas was used (H_2O, CO_2 and SO_2 present), but NO reduction was slightly lower (70 versus 80%) at the same NH_3-to-NO ratio when water vapor and CO_2 were present.

Table 31 summarizes some of the data on temperature, space velocity, and short-term SO_2 effects on the activity of vanadia for the selective NO reduction with NH_3. Table 32 presents additional space velocity effect data as well as data generated on the effects of NO and NH_3 concentration. The following conclusions can be drawn from these data concerning the selective NO reduction with ammonia on the Harshaw V_2O_5 catalyst (NA-25):

- The optimum reaction temperature appears to be at or near 400°C (Runs 1 through 5, Table 31).
- NO reduction increased with decreasing space velocity in the range of 20,000 hr^{-1} to 10,000 hr^{-1} (STP); additional space velocity reduction, e.g., to 5,000 hr^{-1}, did not appear to influence NO reduction. The space velocity effect was observed at all NO concentrations and NH_3-to-NO ratios used (Run 7, Table 31 indicated abnormally low NO conversion when compared to data obtained with similar NH_3-to-NO ratios at 10,000 hr^{-1}, Table 32).
- NO concentration in the range of 250 to 1000 ppm had little or no effect on NO reduction to N_2 (Table 32).

Table 31. TEMPERATURE, SPACE VELOCITY AND SHORT-TERM SO_2 EFFECTS ON THE REDUCTION OF NO WITH NH_3 ON HARSHAW VANADIA (NA-25)

Run No.	Temperature (°C)	Inlet Gas Composition[a]			Outlet Gas Composition			NO Reduction (%)	Excess NH_3 Usage (%)
		NO (ppm)	NH_3 (ppm)	SO_2 (ppm)	NO (ppm)	N_2O (ppm)	NH_3 (ppm)		
	A. TEMPERATURE AND SPACE VELOCITY EFFECTS:								
1	400	969	670	0	352	0	75	63.7	45
2	310	969	670	0	464	0	146	52.1	56
3	445	969	670	0	352	0	87	63.7	42
4	485	969	670	0	364	0	35	62.4	57
5	400	966	650	0	390	0	87	59.6	47
6	400	960	982	0	325	0	168	66.1	92
7[b]	400	973	944	0	241	0	28	75.2	88
8[c]	400	975	950	0	259	0	124	73.4	73
	B. SO_2 EFFECT:								
9	400	979	668	0	352	0	-	64.0	-
10	400	979	668	1000[d]	352	0	-	64.0	-
11	400	979	410	1000	532	0	-	45.7	-
12	400	992	360	1000	311	0	-	68.6	-
13	400	928	720	0	380	0	-	59.1	-
14	400	936	720	1000	380	0	-	59.4	-
15	400	936	1060	1000	287	0	-	69.3	-
16	400	936	482	1000	508	0	-	45.7	

[a] Feed gas also contains 5% H_2O, 14% CO_2, 3% O_2, in N_2.

[b] Space velocity was 10,000 hr^{-1} (STP) rather than the nominal 20,000 hr^{-1}.

[c] Space velocity was 15,000 hr^{-1} (STP) rather than the nominal 20,000 hr^{-1}.

[d] Each SO_2 test was of at least 1 hour duration.

Table 32. EFFECT OF NO AND NH_3 CONCENTRATION AND SPACE VELOCITY ON THE REDUCTION OF NO WITH NH_3 ON HARSHAW V_2O_5 CATALYST (NA-25)

Run No.	Inlet Gas Composition[a]		Space Velocity Hr^{-1} x 10^{-3} (STP)	Outlet Gas Composition			Conv. of NO (%)	Catalyst Weight (gm)	Excess NH_3 Usage (%)
	NO (ppm)	NH_3 (ppm)		NO (ppm)	N_2O (ppm)	NH_3 (ppm)			
1	340	320	5	0	0	0	100	28	41
2	924	1048	10	20	0	123	97.8	28	54
3	268	285	10	0	0	0	100	28	50
4	281	181	10	103	0	0	63.3	28	52
5	479	336	10	180	0	19	62.4	28	59
6	474	380	10	91	0	N.A.	80.8	28	N.A.
7	517	483	10	0	0	26	100	28	32
8	951	1370	20	259	0	501	72.8	14	89
9	973	1224	20	296	0	373	69.6	14	112
10	285	154	20	157	0	0	44.9	14	81
11	258	154	20	135	0	0	40.3	14	88
12	258	297	20	87	0	N.A.	66.2	14	N.A.
13	1078	827	5	261	0	N.A.	75.8	14	N.A.
14	1128	983	5	126	0	N.A.	88.8	14	N.A.

[a] Inlet gas also contains 14% CO_2, 5% H_2O, 3% O_2 in N_2; 400°C (752°F).

- The value of the NH_3-to-NO ratio in the range of 0.5 to 1.2 had a dramatic effect on the extent of NO reduction; the latter increased with increasing value of this ratio approximately linearly at low space velocities. This effect leveled off at ratio values exceeding 1.2.

- Virtually complete NO reduction to N_2 was attained at 400°C, 10,000 hr^{-1} (STP), and an NH_3-to-NO ratio of 1.2.

- The short-term SO_2 effect on NO conversion was negligible or nonexistent (Table 31, Runs 9 through 16).

Figure 23 illustrates most of the above effects and the justification of the conclusions drawn.

Long term SO_2 effects were investigated at low space velocities in order to reduce synthetic flue gas consumption. The same sample of catalyst (NA-25) was subjected to SO_2 containing flue gas (1200 to 1500 ppm) for over 50 hours. No detectable catalytic activity deterioration was observed during these tests. The data is summarized in Table 33.

4.5.3 Iron-Chromium Oxide Catalysts

Several iron-chromium oxide catalysts were screened for activity in the selective reduction of NO by NH_3. By far the most promising proved to be two UCLA catalysts prepared by impregnation of alumina with aqueous solutions of iron and chromium nitrates and from solutions of iron nitrate and chromium trioxide, respectively. Whether their superiority over similar commercial catalysts was due to composition differences or to method of preparation is not known.

Under screening tests conditions (400°C, 20,000 hr^{-1}) these catalysts (NA-28 and NA-29) promoted NO reduction by nearly 70%. This extent of NO conversion represented the highest value attained on any of the 36 catalysts screened. Thus, NA-28 and NA-29 were ranked as the prime candidates for additional testing.

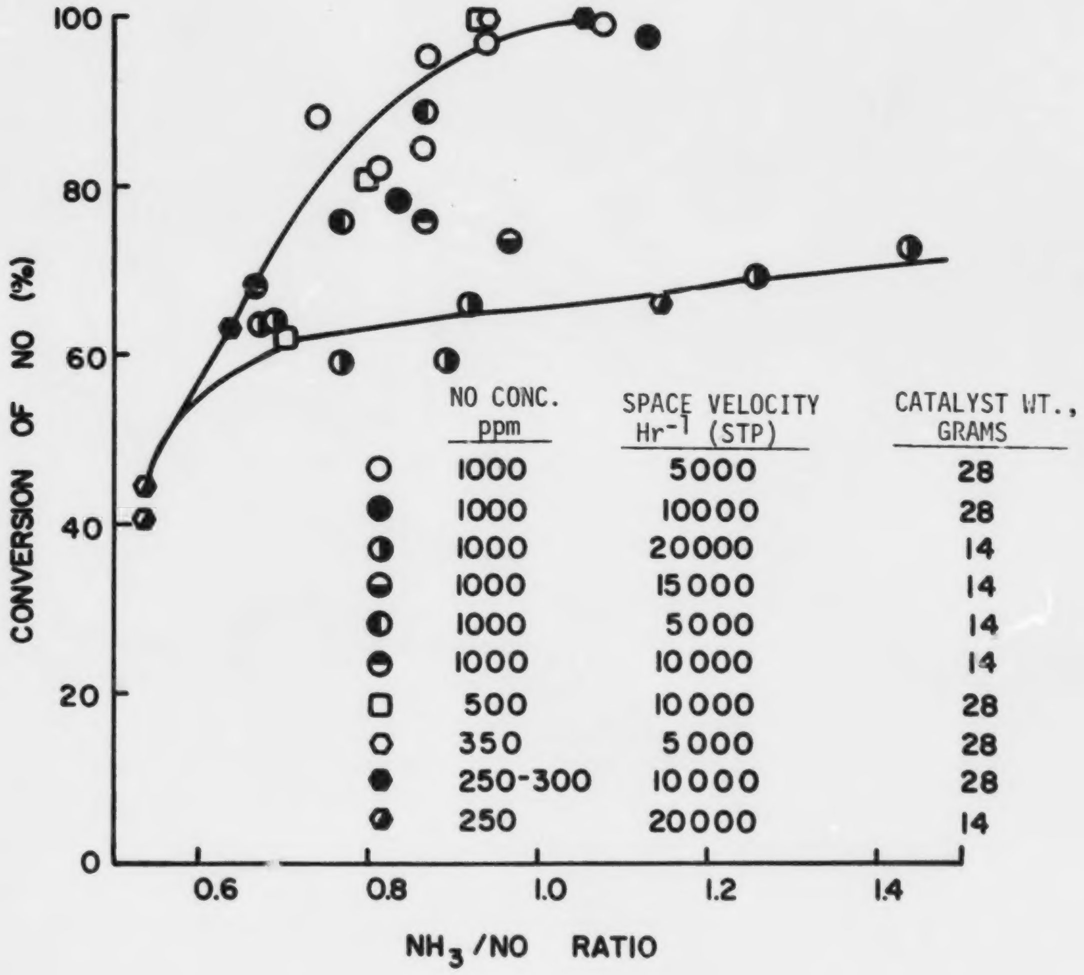

Figure 23. Reduction of NO With NH_3 on V_2O_5 Catalyst at 400°C; 14% CO_2, 5% H_2O, 3% O_2 in N_2)

Table 33. LONG-TERM SO_2 EFFECT ON THE CATALYTIC ACTIVITY OF VANADIA FOR THE SELECTIVE NO-NH_3 REACTION

Run No.	Inlet Gas Composition[a] NO (ppm)	NH_3 (ppm)	SO_2 (ppm)	Space Velocity $Hr^{-1} \times 10^{-3}$ (STP)	Outlet Gas Composition NO (ppm)	N_2O (ppm)	NH_3 (ppm)	Conv. of NO	Excess NH_3 Usage (%)
1	1084	946	0	5	52	0	0	95.2	38
2	1084	946	1500	5	99	0	0	90.9	44
3[b]	1175	1040	1500	5	166	0	0	85.9	55
4[c]	1130	840	1500	5	152	0	0	86.5	29
5	1130	840	0	5	131	0	0	88.4	26
6	1040	698	0	10	332	0	0	68.1	48
7	1014	847	0	10	221	53	0	78.2	50
8	1018	1096	0	5	8	62	66	99.2	54
9	1016	881	0	5	155	0	0	84.7	53
10	1043	841	0	5	185	0	0	82.3	47
11[d]	1043	841	1200	5	185	0	0	82.3	47
12	1026	965	0	5	28	0	0	97.3	45
13[e]	1040	1035	1200	5	38	0	0	96.3	55

[a] Inlet gas also contained 3% O_2, 5% H_2, 14% CO_2 in N_2. All runs were performed at 400°C. 28 gm catalyst used.

[b] 4 hour test (normally data points were taken after one hour of steady-state operation).

[c] 6 hour test.

[d] 19 hour test.

[e] 25 hour test.

The parametric investigations performed on these catalysts involved temperature, NO concentration, NH_3-to-NO ratio, space velocity, and SO_2 effects on NO reduction by NH_3; long-term SO_2 effects were performed only on NA-28. The data are summarized in Tables 34 and 35.

The data in these tables indicate that the two Fe-Cr oxide catalysts showed the same activity for the selective NO reduction and the same sensitivity, or insensitivity, to important reaction parameters. The data generated on the Fe-Cr catalysts is also practically identical to that generated on vanadia. Thus, the conclusions drawn on the vanadia apply to these catalysts also. Important parameters to NO conversion were: (a) temperature, with the optimum value being near 400°C, (b) NH_3-to-NO ratio, with its optimum value being between 1.0 and 1.2, and (c) space velocity, with an optimum value of about 10,000 hr^{-1} (STP).

The NA-28 catalyst was exposed for over 70 hours to SO_2 containing flue gas (1,000 to 1,500 ppm) under a number of different experimental conditions with no discernable effect on its activity for the NH_3-NO reaction (Table 35).

Figure 24 presents the 400°C parametric study data on these catalysts and graphically illustrates the similarity of these catalysts. Furthermore, comparison of Figures 23 and 24 clearly shows the similarity between the Fe-Cr oxide and vanadia catalysts. As was the case with vanadia, these catalysts did not promote N_2O production either.

Their was one exception to the apparent complete similarity between these two catalysts and vanadia which could be potentially significant. The NA-28 catalyst at low space velocities (10,000 hr^{-1} or lower) appeared to completely decompose (or oxidize) the excess ammonia in the system, regardless of the value of the NH_3-to-NO ratio. This can be interpreted as a disadvantage because excess ammonia consumption is higher than with NA-29 or vanadia where most of the ammonia not used by the NO is present in the reactor effluent gas. To be of value, however, the ammonia must be recovered from the flue gas stream and such recovery is highly unlikely to

Table 34. PARAMETRIC INVESTIGATIONS ON Fe-Cr OXIDE CATALYSTS EMPLOYED IN SELECTIVE REDUCTION OF NO WITH NH_3

Run No.	Inlet Gas Composition[a] NO (ppm)	Inlet Gas Composition[a] NH_3 (ppm)	Space Velocity ($Hr^{-1} \times 10^{-3}$ (STP))	Outlet Gas Composition NO (ppm)	Outlet Gas Composition NH_3 (ppm)	Outlet Gas Composition N_2O (ppm)	Conv. of NO (%)	Excess NH_3 Usage (%)	Reaction Temperature (°C)
	CATALYST NA-28								
1	931	915	20	223	97	0	76.0	73	400
2	952	553	20	529	68	0	44.4	72	400
3	870	1093	20	228	352	0	73.8	73	400
4	879	759	20	446	370	0	49.2	35	325
5	879	759	20	323	112	0	63.3	75	400
6	907	942	20	223	119	0	75.4	80	400
7	907	942	20	318	257	0	64.9	74	350
8	907	942	20	233	0	0	74.3	110	450
9	907	890	20	372	0	0	59.0	150	500
10	893	1110	10	46	0	0	94.8	97	400
11	966	900	20	200	0	N.A.	76.6	N.A.	400
	CATALYST NA-29								
1	915	1107	10	554	871	0	39.5	-2	260
2	915	1107	10	90	286	0	90.2	49	350
3	915	1107	10	124	39	0	86.4	103	450
4	945	980	20	256	159	0	72.9	79	400
5	970	1147	20	242	237	0	75.1	87	400
6	519	693	20	119	N.A.	0	77.1	N.A.	400
7	266	337	20	60	73	0	77.4	93	400
8	998	730	20	326	189	0	67.3	21	400
9	967	863	10	128	158	0	86.8	26	400
10	979	635	10	261	124	0	73.3	7	400
11	965	1081	10	95	312	0	90.2	33	400
12	886	1107	10	68	203	0	92.3	66	400
13	1004	725	20	320	N.A.	0	68.1	N.A.	400
14	1004	1120	20	190	N.A.	0	81.1	N.A.	400

[a] Inlet gas also contains 14% CO_2, 3% O_2, 5% H_2O in N_2.

Table 35. REDUCTION OF NO WITH NH_3 ON Fe-Cr CATALYST (NA-28) IN THE PRESENCE OF SO_2

Run No.	Inlet Gas Composition[a]			Space Velocity (hr^{-1} STP)	Outlet Gas Composition			Conv. of NO (%)
	NO (ppm)	NH_3 (ppm)	SO_2 (ppm)		NO (ppm)	NH_3 (ppm)	N_2O (ppm)	
1	1041	887	0	10	176	0	0	83.1
2	1055	1231	0	5	18	0	0	98.3
3	1055	987	0	5	86	0	0	91.8
4	1055	770	0	5	245	0	0	76.8
5	929	915	0	5	95	0	0	89.8
6[b]	969	915	1200	5	99	0	0	89.8
7	981	938	0	5	57	0	0	94.2
8	981	1129	0	5	0	0	0	100
9	969	673	0	5	325	0	0	66.5
10[c]	1040	960	1200	5	100	0	0	90.4
11	996	858	0	10	132	0	0	86.7
12	1015	1012	0	15	77	0	0	92.4
13	1015	898	0	15	170	0	0	83.3
14[d]	1061	898	1000	15	168	0	0	84.2
15	1089	740	0	5	220	0	0	80.0
16[e]	1089	740	1400	5	241	0	0	77.9
17[f]	982	840	1400	5	156	0	0	84.1
18[g]	977	840	1400	5	174	0	0	82.2
19[h]	977	840	1400	5	172	0	0	82.2
20[i]	907	868	0	5	34	0	0	96.3
21[j]	907	868	1500	5	57	0	0	93.7
22	940	767	0	20	309	79	0	67.1

[a] Feed gas also contains 3% O_2, 5% H_2O, 14% CO_2 in N_2. All tests were performed at 400°C.

[b] 7 hour test.

[c] 4 hour test.

[d] 5 hour test.

[e] 2 hour test.

[f] After 20 hours exposure to SO_2.

[g] After 23 hours exposure to SO_2.

[h] After 42 hours exposure to SO_2.

[i] After overnight exposure to air at 400°C.

[j] After 7 hours exposure to SO_2 in this test. Total exposure in series, 49 hours. Total exposure of catalyst to SO_2 in all tests, 71 hours, including preliminary qualitative tests.

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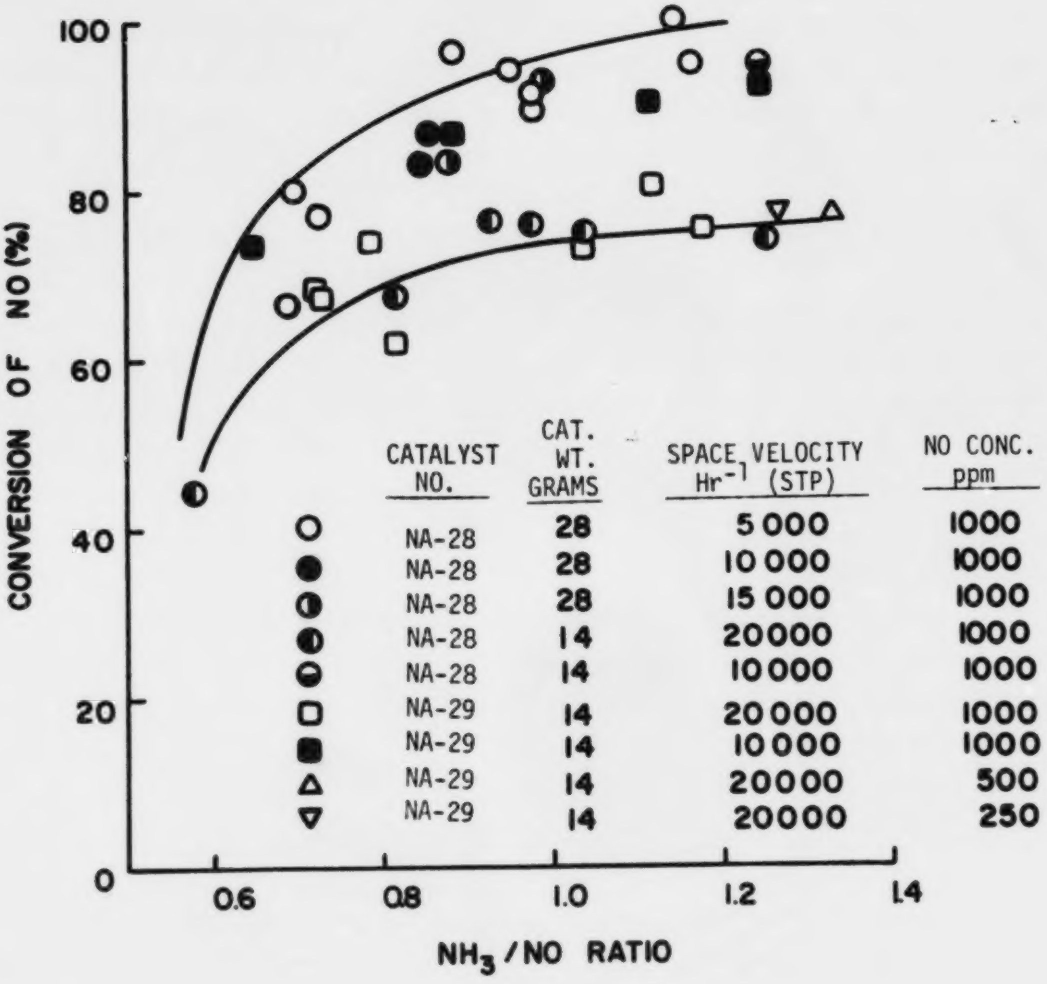

Figure 24. Reduction of NO with NH_3 on Fe-Cr Catalysts at 400°C (14% CO_2, 5% H_2O, 3% O_2 in N_2)

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prove cost effective. But the ammonia in the reactor effluent may have to be recovered for air pollution control reasons. Should this be the case the NA-28 must be considered as the most desirable catalyst for NO_x abatement in power plants through selective NO reduction. No other catalyst tested in this program or reported in the literature combined efficient NO reduction with ammonia in the presence of oxygen and SO_2 and complete decomposition of the excess ammonia.

4.6 PRIORITIZED LISTING OF NO_x ABATEMENT CATALYSTS BASED ON TASK 2 INVESTIGATIONS

The experimental investigations on NO_x abatement catalysts performed under this program identified one catalyst, Pt, potentially useful in NO decomposition and several catalysts which promoted the selective NO reduction by NH_3 in the presence of oxygen and sulfur dioxide. Only catalysts that indicated substantial activity in one of the catalytic NO_x abatement processes at temperatures of 400°C (752°F) or lower were considered. These catalysts are listed below (Table 36) in the order ranked, with the top ranked catalyst listed first. The catalysts are ranked separately for utilization in power plants whose flue gas contains SO_2 and for utilization with virtually SO_2-free flue gas. The most probable temperature and space velocity for optimum catalyst performance are indicated also.

The top ranked catalysts in the two groups were selected as promising candidates for use in power plant NO_x abatement, especially for existing power plants. Thus, a preliminary design and cost analysis of their adaptation to power plants was performed in Task 3.

Efficient catalysts for selective or nonselective NO reduction with H_2 or CO were not identified during the screening tests (400°C, 20,000 hr^{-1}) of Task 2.

Table 36. CATALYST RANKING BASED ON TASK 2 DATA

Cat. Rank	Cat. No. and Active Components	Intended Process	Expected Operation		Expected NO Conv., %
			Temp., °C	S.V., Hr^{-1} (STP)	
	A. UTILIZATION WITH SO_2-CONTAINING FLUE GAS				
1	NA-28, Fe-Cr Oxides	NH_3 Red.	350-400	10,000-15,000	>90%
2	NA-29, Fe-Cr Oxides or NA-25, V_2O_5	NH_3 Red. NH_3 Red.	350-400 350-400	10,000-15,000 10,000-15,000	>90% >90%
3[a]	NA-7, Mo-Oxide or NA-18, CuO-Pb or NA-33, Fe-Oxide	NH_3 Red.	350-400	~10,000	>80%
4[a]	NA-2, 0.5% Pt or NA-4, Pt-Mo	Decomp. Decomp.	300 350	~10,000 ~10,000	>50% >50%
	B. UTILIZATION WITH SO_2 - FREE FLUE GAS				
1	NA-2, 0.5% Pt	NH_3 Red.	200-250	~20,000	>90%
2	NA-28, Fe-Cr Oxide	NH_3 Red.	350-400	~10,000	>90%
3	NA-29, Fe-Cr Oxide or NA-25, V_2O_5	NH_3 Red.	350-400 350-400	~10,000 ~10,000	>90% >90%
4	NA-2, 0.5%Pt	Decomp.	300	~10,000	>50%

[a] Not tested with SO_2-containing flue gas, but indirect evidence leads to expectation of negligible SO_2 effect on catalytic activity.

5. EVALUATION OF THE COST EFFECTIVENESS IN THE USE OF CATALYSTS TO REDUCE NO_x EMISSIONS FROM POWER PLANTS (TASK 3)

The objective of this task was to conduct a preliminary design and cost analysis on catalytic NO_x abatement processes assessed as potentially adaptable to power plants on the basis of information collected in Tasks 1 and 2 (Sections 3 and 4 of this report).

Review of the literature, including unpublished work (Task 1) and of the experimental data generated under this program (Task 2) suggested the following:

- Truly efficient catalysts that can potentially perform in power plant flue gas environment have only been identified for nonselective NO_x reduction and for selective NO_x reduction with ammonia.

- For the majority of power plants (power plants fired with sulfur containing fuels) a simultaneous NO_x-SO_x abatement scheme is the most desirable. The nonselective NO_x-SO_x reduction schemes appear to be the most promising in this category. Preliminary data presented in Section 3.3 indicate that simultaneous NO_x-SO_x reduction is feasible. In one case, NO_x was completely reduced to nitrogen while approximately 80% of the SO_x was simultaneously reduced to elemental sulfur without measurable production of H_2S or COS (NYU catalyst); in a second scheme, NO_x and SO_x were virtually completely reduced to nitrogen and recoverable metallic sulfides in a single reactor (TRW Sulfide Process). In both cases coal can be used as the reductant. The major question marks with these schemes concern the difficulty and cost of adaptation to existing power plants.

- For the small number of power plants expected to continue to use sulfur-free or very low sulfur fuels, the selective NO_x reduction with NH_3 on Pt process may be more desirable. This process has demonstrated high efficiency at low temperatures (~200°C)

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- For existing power plants (fired with sulfur containing fuels) for which a nonselective catalytic process is not desirable because of design incompatibility or because the power plant is already equipped with SO_x scrubbers, or for power plants located in areas where fuel is scarce of too expensive, the selective NO_x abatement by ammonia on non-noble metal catalysts is indicated (e.g., Fe-Cr oxides or V_2O_5).

Current and projected fuel costs suggest that the candidate nonselective NO_x-SO_x abatement process must be capable of utilizing the lowest possible grade of fuel as the process reductant and that the process adaptation scheme should be such that complete and efficient energy utilization is possible.

Reductant generation at the boiler burner by fuel-rich combustion has not been possible with fuels other than natural gas, to our knowledge. But even if possible with some fuels, it would be difficult to control the oxidant-reductant ratio at the precise value required by the simultaneous catalytic NO_x-SO_x process.

The use of piped natural gas, CO, or H_2 could be the most desirable reductant source technically, but the scarcity and cost of these fuels render it unfeasible for general adaptation.

Reductant generation on the power plant site, preferably as an integral part of the process, by a relatively inexpensive fuel, such as coal, appears to be the desirable reductant source. Thus, a scheme involving two-stage combustion would be desirable.

On the basis of the above input, the following five processes were selected for preliminary design and cost analysis:

1. One simultaneous catalytic NO_x-SO_x reduction process, utilizing coal as the reductant, for adaptation to new power plants.
2. One simultaneous NO_x-SO_x catalytic reduction by coal process for adaptation to existing power plants.

3. One simultaneous NO_x-SO_x reduction process, catalytic with respect to NO_x and either throwaway or regenerative with respect to SO_2, for new power plants (TRW Sulfide Process).

4. One selective NO_x reduction with NH_3 on non-noble metal catalysts process for either new or existing power plants.

5. One selective NO_x reduction with NH_3 on platinum process for new or existing power plants.

The next two sections of this report present the bases for the design and cost evaluation of these five NO_x abatement processes and summarize the engineering analysis results. The processes are treated in two groups, simultaneous NO_x-SO_x reduction processes and selective NO_x reduction with ammonia processes. Specifics on individual processes are presented in separate subsections of the appropriate section.

5.1 PRELIMINARY DESIGN AND COST ANALYSIS OF SIMULTANEOUS NO_x-SO_x REDUCTION SCHEMES

Processes 1 and 2 above were assumed adapted to power plants by the TRW schemes, conceptual diagrams of which are presented in Figures 14a and 14b (Section 3.3). The TRW schemes were selected because they are believed to be very efficient schemes, which can utilize any type of inexpensive fuel as the reductant source, and because they are the only schemes on which data were available. It was also assumed that a single-stage catalytic reactor would be sufficient for adequate NO_x-SO_x reduction. This assumption implies that H_2S and COS production on the catalyst does not take place or, if it does, it is at levels acceptable for atmospheric discharge; such catalyst has been identified (Table 14, Section 3.3) by NYU. The catalytic reactor was sized on the basis of TRW generated data on a Harshaw CuO catalyst (Table 16, Section 3.3) because the NYU data was insufficient and it also arrived late. However, the deductions drawn from the engineering analysis of these processes would not be affected materially by a catalyst switch such as the one contemplated here (both catalysts are non-noble metal catalysts). The catalytic reactor design was based on Monsanto's reactor design for the CATOX Process.

Process 3, the "TRW Sulfide Process" which was presented in Section 3.3 (Figure 16), does not require a catalytic reactor. The catalyst for the NO_x reduction is the sulfur product getter (if not the coal), which for the purpose of this analysis was iron (it is believed that iron oxide or other metal oxides may be used). Thus, the reductant generator and the catalytic reactor are a single unit in this simultaneous NO_x-SO_x abatement approach. The product iron sulfide was treated as a waste because of lack of data on a regenerative process for the sulfur getter. The process engineering analysis on this scheme was based on limited proof-of-principle data generated earlier at TRW (Section 3.3, page 67).

The analyses were based on process adaptation to an 800 MW power plant (320 tons/hr coal consumption on boiler burners and reductant generator combined) except for Process 2 (NO_x-SO_x catalytic reduction scheme for existing plants), where the electric generating capacity exceeded 800 MW by the quantity of power produced from the reductant generator coal.

Table 37 lists the assumed composition of the reductant coal.

Table 37. ASSUMED CHEMICAL COMPOSITION FOR THE REDUCTANT COAL, WEIGHT PERCENT

Carbon		70
Hydrogen		5
Oxygen		10
Sulfur		3
Ash		11
Nitrogen		1
	Total	100% (Dry Basis)

Moisture Content 4%

Water oxygen = (4) (16/18) = 3.6%
Water hydrogen = (4) (2/18) + 0.4%
Non-water hydrogen = 5 - 0.4 = 4.6%
Non-water oxygen = 10 - 3.6 = 6.4%

Based on the Dulong formula* a coal of this composition would have a heat content of 12,628 Btu/lb.

The flue gas production in the primary burner was assumed to be 281,250 standard cubic feet (60°F and 1 atmosphere) per ton of coal consumed (90 x 10^6 SCFH from a power plant consuming 320 tons per hour of coal). Table 38 presents the assumed power plant flue gas composition.

Table 38. ASSUMED POWER PLANT FLUE GAS COMPOSITION (VOLUME %)

N_2	75
CO_2	14.5
H_2O	7.0
O_2	3.0
SO_2	0.2
NO_x	0.1
Fly ash, etc.	0.2
Total	100%

Because of the extraordinarily large size of some of the required equipment (e.g., fans, reaction vessels) and the uniqueness of some of the applications (e.g., internal insulation of large ducts to carry high temperature flue gas), many of the capital cost items could not be estimated from the data reported in the literature (e.g., by Guthrie[1]) for smaller size industrial units. Accordingly, the estimated capital costs for many of the process scheme components had to be obtained from equipment manufacturing firms and supply houses. Table B-1 in Appendix B of this report contains a partial listing of the various companies contacted.

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* Btu/lb = 14,544 C + 62,028 (H - O/8) + 4050 S where C, H, O, and S are in fractional weights.

The f.o.b. equipment costs were adjusted to include estimates of installation costs, project indirect costs, and contingencies. Except where the equipment manufacturers suggested a lower value, the installation cost was estimated at 58% of the f.o.b. equipment cost. This is in line with the data by Guthrie which indicate that labor costs for equipment installation and for erection of field materials range from 54 to 66% of the equipment cost, with the "norm" being close to 58%. The installation costs for fans and multiclones were estimated at 30% of the equipment cost. In accordance with the data reported by Guthrie, the project indirect costs and contingencies were estimated at 34% of the installed equipment costs and 18% of the project cost, respectively. The estimates of the total operating cost include the following: a 10-year straight line depreciation cost; an 8% of the capital investment per year allowance for maintenance, insurance, local taxes, etc.; labor cost with 100% overhead; heat losses and power consumption costs; and, where applicable, costs for the two NO_x-SO_x catalytic reduction processes and for the modified process for SO_x removal, no credit was allowed for the recovered by-products (sulfur and ferrous sulfide, respectively).

The next three subsections present the design and cost data generated on each of the three simultaneous NO_x-SO_x processes. Process 1, catalytic NO_x-SO_x process for existing power plants, is discussed in considerable detail; the other two schemes, which contain a number of similar elements to Process 1, are discussed in less detail. Details and support data on the analysis of these schemes are presented in Appendix B of this report.

5.1.1 Simultaneous Catalytic NO_x-SO_x Reduction Scheme-New Power Plants

Figure 25 presents a schematic flow diagram for the application of the NO_x-SO_x Catalytic Reduction Process to new power plants (gas flow rates, etc., shown on the figure will be discussed later). A portion of the hot boiler flue gases, generated at the power plant burners (primary combustion), are diverted from the secondary superheater boiler region to a coal bed ("Reductant Generator") which is also fed with a fraction of the total coal to be consumed by the power plant in the generation of the 800 MW power. The oxygen in the flue gas reacts with the coal in the coal bed to generate carbon monoxide,

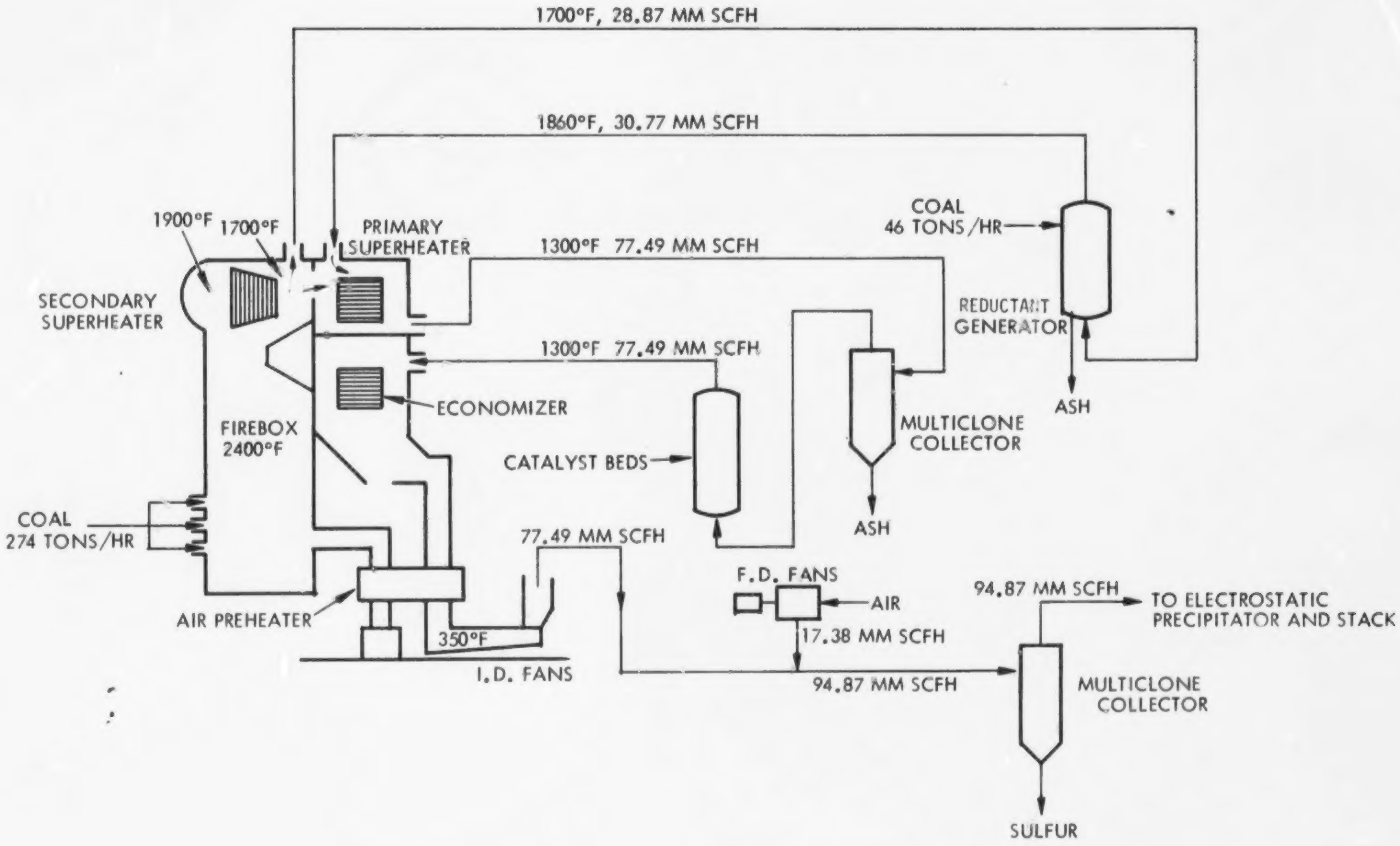
1700°F, 28.87 MM SCFH
1860°F, 30.77 MM SCFH
1900°F
1700°F
PRIMARY SUPERHEATER
1300°F 77.49 MM SCFH
COAL 46 TONS/HR
SECONDARY SUPERHEATER
REDUCTANT GENERATOR
1300°F 77.49 MM SCFH
ECONOMIZER
ASH
FIREBOX 2400°F
MULTICLONE COLLECTOR
CATALYST BEDS
COAL 274 TONS/HR
ASH
77.49 MM SCFH
F.D. FANS
AIR
94.87 MM SCFH
TO ELECTROSTATIC PRECIPITATOR AND STACK
AIR PREHEATER
350°F
17.38 MM SCFH
I.D. FANS
94.87 MM SCFH
MULTICLONE COLLECTOR
SULFUR

Figure 25. NO_x-SO_x Catalytic Reduction Process Adapted to New Power Plants (800 MW)

$$C + 1/2\ O_2 \rightarrow CO \tag{1}$$

Other major reactions taking place in the reductant generator include oxidation of the organically-bound hydrogen and (some) reduction of water and carbon dioxide,

$$2\ (-H) + 1/2\ O_2 \rightarrow H_2O \tag{2}$$

$$C + H_2O \rightarrow CO + H_2 \tag{3}$$

$$C + CO_2 \rightarrow 2\ CO. \tag{4}$$

The oxygen-free reductant-rich effluent gas from the CO generator is mixed in the primary superheater section of the boiler with the undiverted portion of the flue gas. Through proper system design the two gas streams can be so proportioned that the mixing would result in the reduction of all the oxygen and in the oxidation of all the hydrogen and carbon monoxide, except for a small quantity of CO needed in a subsequent catalytic step for the stoichiometric reduction of sulfur and nitrogen oxides. This would eliminate possibilities for carbon monoxide discharge to atmosphere and for catalyst poisoning by excess oxygen. The reactions involved are as follows:

$$CO + 1/2\ O_2 \rightarrow CO_2 \tag{5}$$

$$H_2 + 1/2 \rightarrow H_2O \tag{6}$$

Homogeneous oxidation of carbon monoxide and hydrogen and removal of oxygen (in the boiler)

$$2CO + SO_2 \rightarrow 2\ CO_2 + 1/n\ S_b \tag{7}$$

$$CO + NO \rightarrow 1/2\ N_2 + CO_2 \tag{8}$$

Catalytic reduction of nitrogen and sulfur oxides (in the catalytic reactor)

Except for small quantities of heat lost to the surrounding and discharged in the ash, the gaseous effluent from the reductant generator contains essentially all the heat value of the coal fed to this unit. This heat, which is represented by the small rise in the diverted gas temperature and by the fuel value of CO and H_2 carried by this gas, is extracted by the boiler heat exchangers (superheaters, etc.).

As indicated in Figure 25, following the reduction of nitrogen and sulfur oxides in the catalytic reactor, the flue gas is diverted through the economizer and air preheater (for further extraction of heat) to a sulfur recovery system. In this system the sulfur vapor is condensed by direct air injection (cooling) and recovered in cyclone collectors.

The scheme design criteria were established from the data generated by TRW in the apparatus depicted schematically in Figure B-1 (Appendix B). The pertinent information derived from the proof-of-principle data, taken with synthetic flue gas on packed coal and catalyst beds, may be summarized as follows:

- Efficient generation of reductants requires coal bed temperatures in excess of 900°C (1650°F), although reductant generation is possible at lower temperatures. The utilized space velocity range was 1,000-1,500 hr^{-1}.

- The quantity of reductants generated in the coal bed can easily be controlled by the size of the fraction of the flue gas diverted to it, the space velocity of the feed flue gas (residence time in the bed) and the coal bed temperature.

- At temperatures up to 1650°F, the principal source of reductants is coal oxidation by flue gas oxygen and water (Reactions 1 and 3 above). At higher temperatures, a substantial portion of the CO is produced from the reaction of flue gas CO_2 with coal (Reaction 4). At a temperature of 1700°F the estimated percent contributions to the total CO production from Reactions 1, 3 and 4 are 45, 29, and 26, respectively.

- The NO_x and SO_x in the diverted flue gas are totally reduced in the coal bed. The nitrogen oxides are reduced to N_2 and NH_3 with the latter decomposing to N_2

increases with the coal feed rate, and since only stoichiometric quantities of CO and H_2 would be required for reaction with oxygen, NO_x, and SO_x in the undiverted portion of the flue gas, the fraction of the gas diverted to the coal bed would, in turn, depend on the coal feed rate for the CO generator. Only when the diverted and undiverted fractions of the flue gas are at a right proportion will not excess oxygen reach the catalyst (to "poison" it) and no excess carbon monoxide (an air pollutant) be discharged in the stack gases.

Table 39 presents a summary of the calculated data (coal feed rates and expected level of excess oxygen or CO discharge) for assumed flue gas diversion fractions of 30,33.33, 37.50 and 40%. Items 7 and 8 of this table indicate that the optimum fraction of diverted flue gas is approximately 37.5% of total (near zero oxygen and no CO in stack gas). The other three values of diverted flue gas result either in excess oxygen, which would poison the catalyst, or excess CO, which is a pollutant. Thus, 37.5% flue gas diversion was selected as the design value (28.87 MM SCFH diverted gas flowrate). This flow rate requires a coal feed rate of 46 tons/hr. to the reductant generator. Since an 800 MW consumes 320 tons/hr. coal, the coal feed rate to the primary burners is 274 tons/hr. Table B-2 (Appendix B) presents detailed mass balance calculations for the 37.5% diverted flue gas fraction.

Heat balance calculations, based on 37% flue gas diversion, indicated that the heat release in the reductant generator would be 1.85 x 10^8 Btu/hr which would cause an increase in the temperature of the diverted gas from 927°C (1700°F) to 1016°C (1860°F); heat transfer losses were considered negligible. Analogous calculations on the catalytic reactor revealed that no appreciable change in temperature is expected in this unit. The quantity of air necessary to cool the flue gas from 177°C(350°F) to 138°C (280°F) in the elemental sulfur recovery unit was estimated at 17.38 MM SCFH (60°F).

Changes in flue gas flow rates (minor) due to change in flue gas composition (Reactions 1 through 8) are indicated in Figure 25.

Unit sizing was not optimized, but an attempt was made to select dimensions that did not result in high pressure drops. The reductant generator was designed as four circular units, each 30 feet in diameter and H_2 or oxidizing to N_2 and H_2O in the boiler. The sulfur oxides are reduced to elemental sulfur, H_2S and COS at the approximate ratio of 6:3:1, but they reoxidize to SO_2 in the boiler prior to entering the catalyst. The inorganic sulfur content of the coal in the reductant generator remains as pyrite or sulfide in the ash; the organic sulfur of this coal is converted to reduced gaseous sulfur compounds which are carried to the boiler by the diverted flue gas where they oxidize to SO_2.

- The NO_x and SO_x of the combined flue gas stream are reduced on the catalyst bed (Harshaw CuO) to N_2 and S_n (60-70%), H_2S (15-25%, and COS (3-5%), respectively. Recommended operating conditions: 482-704°C (900-1300°F) and 8,000 to 10,000 hr^{-1} space velocity.

The following space parameters were selected for this engineering analysis:

	Reductant Generator	Catalytic Reactor
Temperature	927°C (1700°F)	704°C (1300°F)
Space Velocity	1,500 hr^{-1}	9,000 hr^{-1}

The NO_x and SO_x conversions on the catalyst bed were considered adequate to meet clean air standards so that further treatment of the flue gas, other than elemental sulfur recovery, was not considered necessary. The optimum fraction of flue gas to be diverted to the reductant generator under the selected conditions of temperature and space velocity had to be calculated.

It is apparent from the proof-of-principle results that at operating temperature, the coal feed rate for the CO generator is determined by the quantity of the flue gas (i.e., the amount of oxygen) which is fed to the unit. Since the quantity of reductants (CO and H_2) generated in the coal bed

Table 39. EFFECT OF FLUE GAS DIVERSION RATE ON COAL FEED RATES AND MASS BALANCE RESULTS (Operating Temperature for Reductant Generator 927°C (1700°F))

Flue Gas Diverted to Reductant Generator, % →	30	33.33	37.5[a]	40
1. Coal feed rate to reductant generator, tons/hr	38	42	46	50
2. Coal feed rate to primary burner, tons/hr	282	278	274	270
3. CO produced in the reductant generator, lb-mole/hr	5095	5206	6168	6705
4. Hydrogen produced in the reductant generator, lb-mole/hr	1478	1633	1788	1944
5. Oxygen required ror oxidation of H_2, H_2S, S, and excess CO in the reductant generator effluent, lb-mole/hr	2953	3313	3699	4456
6. Oxygen available in the undiverted flue gas, lb-mole/hr	4388	4262	3804	3600
7. Excess oxygen reaching catalyst, lb-mole/hr (Item 6 minus Item 5)	1435	949	105	0
8. Excess CO discharged in stack gases (Item 5 minus Item 6 multiplied by 2)	0	0	0	912

[a] Table B-2 (Appendix B) presents mass balance calculations for this fraction of diverted flow.

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and 15 feet in total height and containing 7 feet of 1/2-inch coal particles (packed beds).* The estimated operating pressure drop through the bed was calculated to be 10 inches of water.

The catalytic reactor is a 30 feet diameter by 130 feet cylindrical unit depicted in Figure 26. The reactor was based on the Monsanto multi-section design. Each section is ten feet high and contains one foot of catalyst (total catalyst volume 8760 cubic feet). The total pressure drop through the reactor was estimated at 2 inches of water (based on 1/2-inch catalyst cylinders and a bed void fraction of 0.5).

The multiclones selected for the removal of fly ash from the flue gas feed to the catalyst reactor consist of 8 units each with a capacity of 600,000 cfm. The manufacturer's estimate of the pressure drop through the multiclones is 3.1 inches of water. The units are expected to effect 95% fly ash removal (assuming about 5% minus 10 micron particle size). Similar type multiclones (5 units) were assumed for sulfur recovery.

Duct cross sections were determined from assumed linear gas velocities of 2,000 and 3,000 fpm for fly ash laden and fly ash free flue gas, respectively.

Four induced draft and two forced draft fans are used in this scheme. Induced draft fans were recommended by several manufacturers for moving large volumes of hot gas. Each induced draft fan has a capacity of 500,000 cfm working against a total estimated scheme pressure of 15 inches of water at 177°C (350°F). Each of the two forced draft fans, selected for air injection in the sulfur recovery section, has a capacity of 169,000 cfm working against an estimated pressure drop of 2 inches of water.

Although the detailed design for a system (equipment) to divert the hot flue gas through the CO generator has not been worked out, discussions with one manufacturer of flow control equipment indicated that the fabrication of a "non-tight" diversion damper for the proposed application should not pose any major engineering difficulty.

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* A fluidized bed may be a more efficient design.

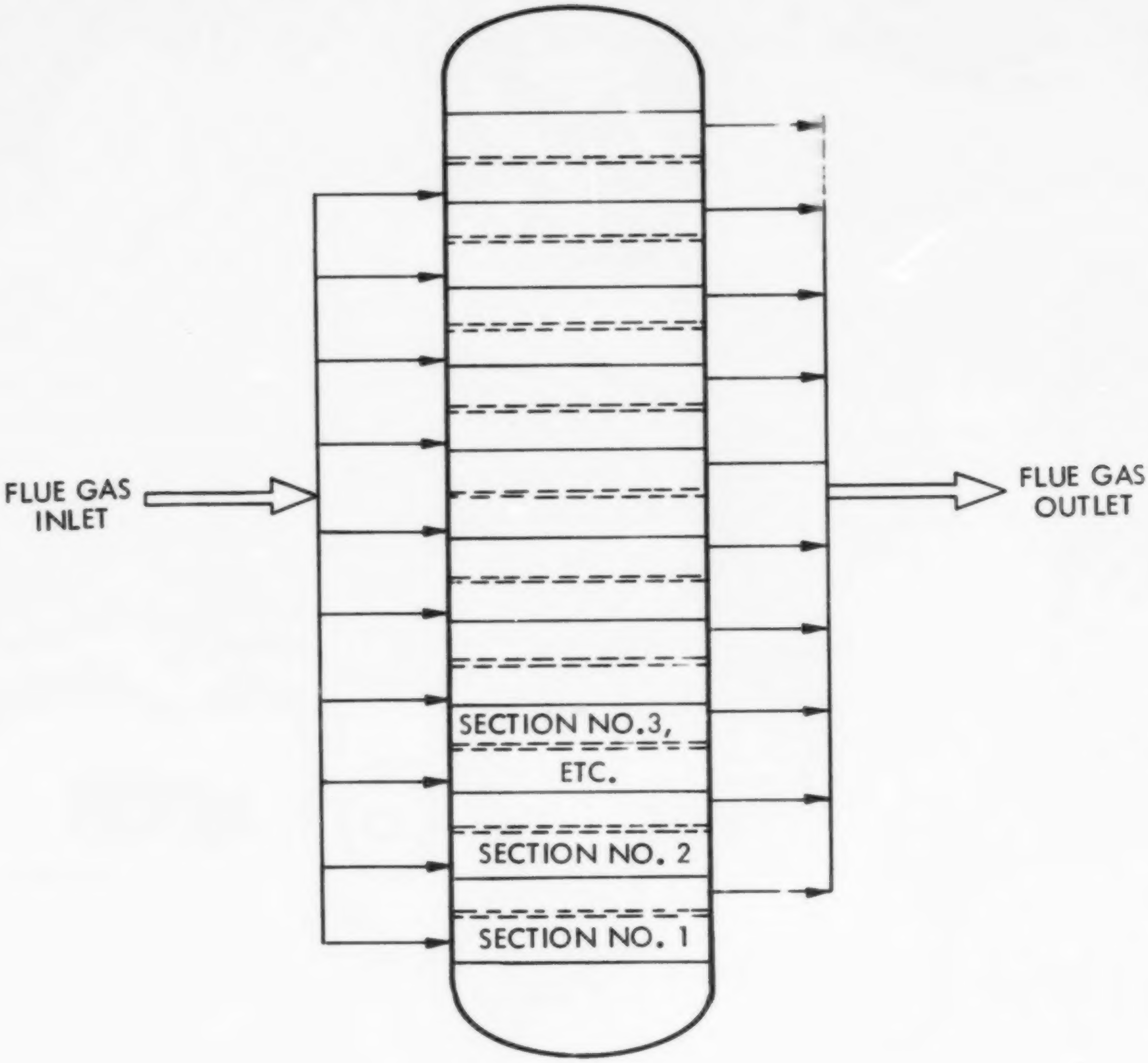
FLUE GAS INLET
FLUE GAS OUTLET
SECTION NO.3,
ETC.
SECTION NO. 2
SECTION NO. 1

Figure 26. Monsanto's Multi-Section Catalytic Reactor

Details on equipment size, type of construction, and unit costs are given in Table B-3 (Appendix B).

Summaries of the estimated capital and operating costs for this scheme (Figure 25) are presented in Tables 40 and 41, respectively. The total capital cost was estimated at $7,305,000 ($9.13 per kw) and the annual operating cost at $2,529,000 (0.040¢ per KWH). Details on these cost estimates are presented in Tables B-3 and B-4 in Appendix B of this report.

5.1.2 Simultaneous Catalytic NO_x-SO_x Reduction Scheme - Existing Power Plants

Figure 27 is a schematic flow diagram depicting the adaptation of the NO_x-SO_x catalytic reduction process to existing power plants. The fraction of the plant effluent flue gas (stack gas, 350°F) diverted to the reductant generator is pre-heated to about 538°C (1000°F) by heat exchange with the hot effluent gas from the catalytic reactor. The oxygen-free, reductant-rich hot gas from the reductant generator is mixed with the undiverted portion of the flue gas (temperature 350°F) and the mixture is sent to the catalytic reactor.

Experimental data on reductant generator performance in the 538°-771°C (1000-1420°F) is not available, but the reactions in the reductant generator, the gas mixing zone (homogeneous reactions), and in the catalytic reactor are expected to be the same as those discussed above for the application of this process to new power plants. However, because of the lower operating temperature of the coal bed, the contributions from Reactions 1, 3, and 4 (Page 4) to the total CO production would be expected to be different. The laboratory experimental results (discussed earlier) had indicated that at temperatures less than 1650°F, Reactions 1 and 3 ($C + 1/2\ O_2 \rightarrow CO$, $C + H_2O \rightarrow CO + H_2$, respectively) would be the principal sources of reductants. For the actual operating temperature of the reductant generator (1000°-1420° range), reactions 1 and 3 were assumed to account for 95% and 5% of the total CO produced, respectively. The coal feed rate to the reductant generator was estimated at 54 tons per hour and the fraction of the flue gas diverted to this unit was calculated to be 0.57. Pertinent computations are presented in Table B-5 (Appendix B).

Table 40. BREAKDOWN OF THE ESTIMATED CAPITAL COST FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR NEW POWER PLANTS (Table B-3 in Appendix B presents details)

	Cost ($000)	
CO Generation Section		
1) Flue gas diversion damper	250	
2) Coal feeder	15	
3) CO generators	480	
4) Ductwork	900	
		1,645
Catalytic Reaction Section		
1) Ductwork	1,200	
2) Multiclones	1,210	
3) Catalytic reactor	1,225	
		3,635
Induced Draft Fans (and Motors)		750
Sulfur Collection Section		
1) Ductwork	630	
2) Multiclones	620	
3) Forced draft fans	25	
		1,275
TOTAL		7,305 (or $9.13/KW)

Table 41. OPERATING COST BREAKDOWN FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR NEW POWER PLANTS (Table B-4 in Appendix B presents details)

	Cost ($000 per year)
1) Depreciation	730
2) Maintenance, insurance, taxes, etc.	584
3) Labor	240
4) Electric power	522
5) Energy losses	168
6) Catalyst replacement	285
TOTAL	2,529 or 0.040 ¢/KWH

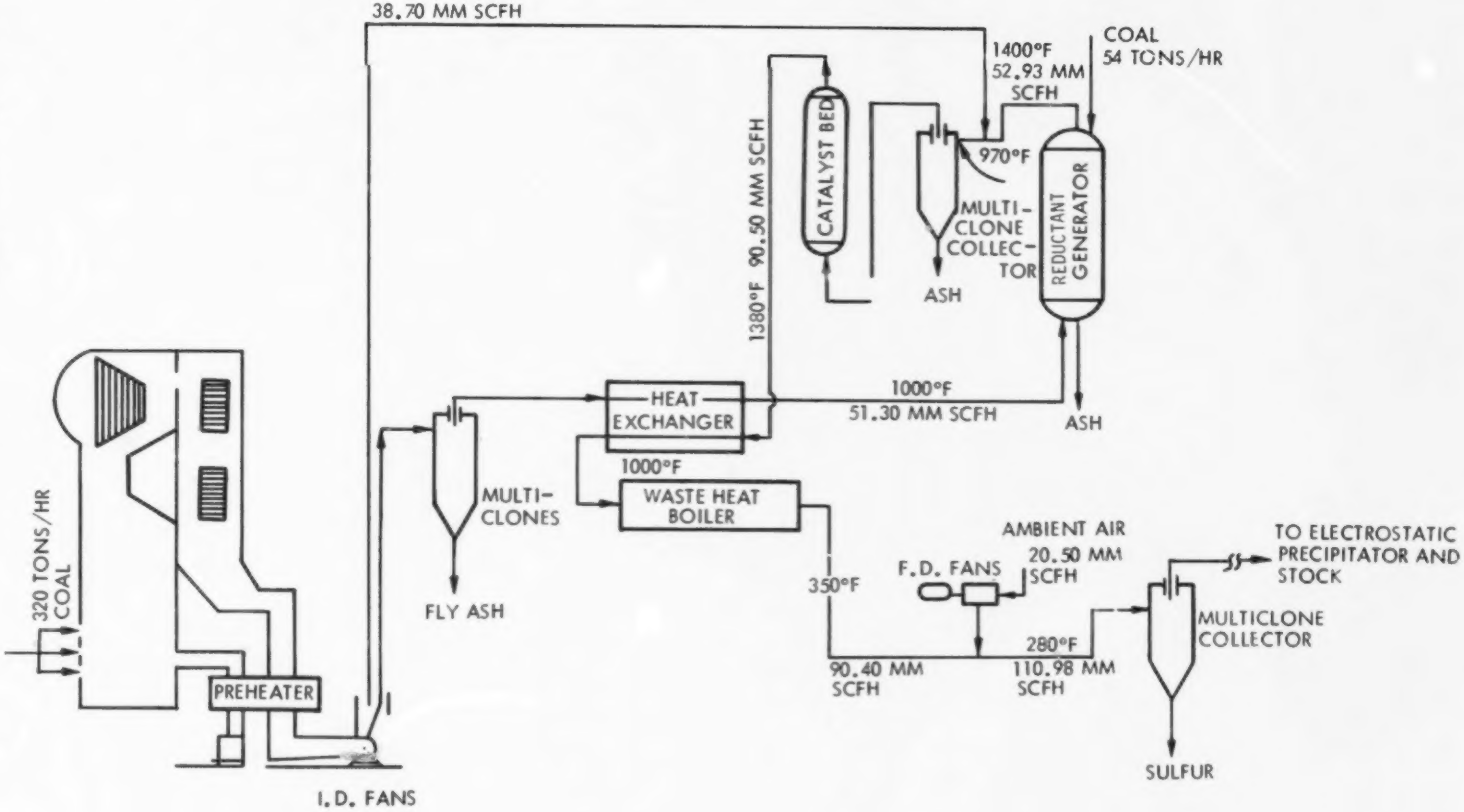
38.70 MM SCFH
1400°F
52.93 MM
SCFH
COAL
54 TONS/HR
CATALYST BED
970°F
MULTI-
CLONE
COLLEC-
TOR
REDUCTANT
GENERATOR
1380°F 90.50 MM SCFH
ASH
ASH
HEAT
EXCHANGER
1000°F
51.30 MM SCFH
1000°F
WASTE HEAT
BOILER
MULTI-
CLONES
FLY ASH
320 TONS/HR
COAL
PREHEATER
I.D. FANS
350°F
AMBIENT AIR
20.50 MM
SCFH
F.D. FANS
TO ELECTROSTATIC
PRECIPITATOR AND
STOCK
MULTICLONE
COLLECTOR
280°F
90.40 MM
SCFH
110.98 MM
SCFH
SULFUR

Figure 27. NO_x-SO_x Catalytic Reduction Process Adapted to Existing Power Plants (800 MW)

A second difference between this scheme and that designed for new power plants involves the energy utilization from the reductant generator coal. In the previous scheme the effluent gas from this unit was returned to the superheater section of the boiler where the energy was absorbed in the normal power plant manner; thus, the coal used in the reductant generator was considered a part of the 120 tons per hour consumption of the 800 MW plant. In this scheme, the energy from the coal consumed in the reductant generator is available for recovery at approximately 538°C (1000°F) after the flue gas exits the heat exchanger. Energy recovery was assumed to take place in a waste heat boiler. This unit was neither sized, nor costed. It was assumed that the cost of the coal fed to the reductant generator (adjusted for losses) and the cost of recovering its energy will equal the credit from the power derived from it. This power was not considered as part of the 800 MW plant capacity; thus, 120 tons per hour coal (or equivalent fuel) was fed to the boiler burning in this scheme.

The procedures used for computing flow rates and gas temperatures at various points in the scheme and for the selection and sizing of equipment are identical to those described for the adaption of the same process to new power plants (Figure 25). Details on equipment sizing, construction materials, and cost are presented in Table B-6 (Appendix B).

Tables 42 and 43 summarize the breakdown of the estimated capital and operating costs for the scheme shown in Figure 27. The data in Table 42 indicate that the heat exchanger unit accounts for a significant portion (48%) of the estimated total capital cost. For this preliminary design, no attempt was made to optimize the exit gas temperature for the unit or to investigate alternate methods for heating the flue gas feed for the reductant generator. Also, the cost of the waste heat boiler was not considered and no credit was taken for the estimated 70 MW of additional electricity generated in this unit (estimate based on an assumed heat extraction efficiency of 20%). Similarly, in estimating the total operating cost, the cost of the 54 tons/hr of coal fed to the CO generator was not considered as an operating expense (refer to earlier discussion). The estimated total capital cost for the process is $14,935,000 (or $18.67 per KW of generating capacity for the main plant boiler) and the estimated

Table 42. BREAKDOWN OF THE ESTIMATED CAPITAL COST FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR EXISTING POWER PLANTS (Table B-6 in Appendix B presents details)

		Cost ($000)	
Reductant Generation Section			
1)	Multiclones	250	
2)	Coal feeder	15	
3)	CO generators	745	
4)	Ductwork	900	
			1,910
Catalytic Reaction Section			
1)	Multiclones	755	
2)	Catalytic Reactor	1,410	
3)	Ductwork	1,470	
			3,635
Sulfur Recovery Section			
1)	Ductwork	690	
2)	Forced draft fans	25	
3)	Multiclones	620	
			1,335
Heat Exchanger			7,120
Induced Draft Fans			935
	TOTAL		14,935 ($18.67/KW)

Table 43. OPERATING COST BREAKDOWN FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS (Existing Power Plants) (Table B-7 in Appendix B presents details)

		Cost ($000/Year)
1)	Depreciation	1,493
2)	Maintenance, insurance, taxes, etc.	1,195
3)	Labor	240
4)	Electric power	575
5)	Energy losses	168
6)	Catalyst replacement	327
		3,998 (0.062¢ per KWH)

annual operating cost is \$3,998,000 (or 0.062¢ per KWH). Details on operating costs are presented in Table B-7 (Appendix B).

5.1.3 Simultaneous NO_x-SO_x Reduction by the TRW Sulfide Process - New Power Plants

In the sulfide process the removal of SO_x from flue gas is achieved by addition of iron scrap and/or iron ore to the reductant generator. The iron-sulfur reaction results in the formation of iron sulfide (FeS and/or FeS_2) which is discharged in the reductant generator ash. The NO_x is reduced by the coal and/or the iron sulfide to N_2. As indicated in Figure 28, the entire flue gas from the plant boiler is passed through the CO generator. The reductant-rich effluent which is devoid of oxygen and free of sulfur compounds is then discharged to the boiler section where addition of a stoichiometric (or an excess) of preheated air results in the oxidation of all the carbon monoxide and hydrogen and release and recovery of energy.

Based on a total plant coal consumption of 320 tons/hr, the coal feed rates for the CO generator and the primary burner were established at 100 and 220 tons/hr, respectively. The procedure used in calculating the feed rates was identical to that presented in Table B-2 of the Appendix for the NO_x-SO_x catalytic reduction process for new power plants. Approximately 15.63 SCFM of air would be required for stoichiometric oxidation of the reductants in the CO generator effluent. The iron required for the process is estimated at 14 tons per hour assuming that sulfur-iron reaction results in the formation of FeS (only 7 tons/hr of Fe would be required if the reaction product is pyrite, FeS_2).

Table 44 presents a summary of the capital cost breakdown for the modified process. The breakdown of the estimated operating cost is shown in Table 45. As indicated in Table 45, 81% of the total operating cost is due to the cost of the iron scrap. In these calculations, the cost of iron scrap was assumed to be \$69/ton. Since in the recent past the price of iron scrap has fluctuated fairly widely, the actual operating cost may be somewhat different than that shown in Table 45, at any given month. In estimating the operating cost, no credit was taken for the product ferrous sulfide (and/or pyrite). The total capital cost for the sulfide process

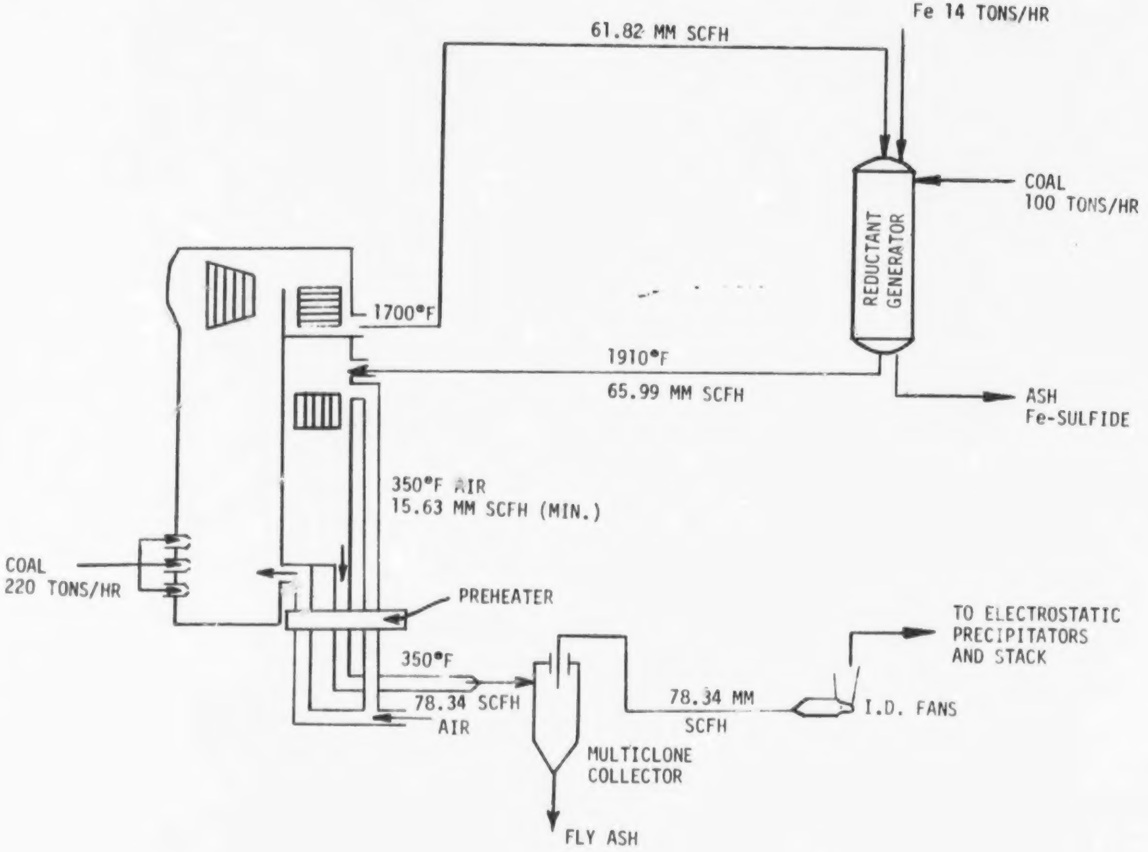
Fe 14 TONS/HR
61.82 MM SCFH
COAL
100 TONS/HR
REDUCTANT
GENERATOR
1700°F
1910°F
65.99 MM SCFH
ASH
Fe-SULFIDE
350°F AIR
15.63 MM SCFH (MIN.)
COAL
220 TONS/HR
PREHEATER
350°F
78.34 SCFH
AIR
TO ELECTROSTATIC
PRECIPITATORS
AND STACK
78.34 MM
SCFH
I.D. FANS
MULTICLONE
COLLECTOR
FLY ASH

Figure 28. Sulfide Process Adaptation to an 800 MW Power Plant

Table 44. BREAKDOWN OF CAPITAL COST FOR THE SULFIDE NO_x-SO_x REDUCTION SCHEME FOR NEW POWER PLANTS (Table B-8 in Appendix B presents details)

	Cost ($000)
Coal/iron feeder	25
Reductant generators	960
Ducts	2,850
Multiclones	495
Induced draft fans	745
	5,075
	(or $6.35/KW)

Table 45. OPERATING COST BREAKDOWN FOR THE SULFIDE NO_x-SO_x REDUCTION SCHEME FOR NEW POWER PLANTS (Table B-9 in Appendix B presents details)

	Cost ($000/Year)
Depreciation	508
Maintenance, insurance, taxes, etc.	406
Labor	160
Electric power	512
Energy losses	168
Iron scrap	7,728
	9,482
	(or 0.15¢ per KWH)

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adaptation to new power plants (800 MW) was estimated at 5,075,000 (or \$6.35 per KW); the annual operating costs were estimated at 9,482,000 (or 0.20¢ per KWH). Details are presented in Tables B-8 and B-9 (Appendix B).

It was pointed out earlier (Section 5.1) that iron ore or other metallic ores may be used instead of iron and that these ores may be regenerable. If iron ore were used in the above computations as a non-regenerable reactant, the annual operating costs would be reduced by \$5 million, even with no credit for the sulfide product. These computations were based at an iron ore price of \$12.16 per ton f.o.b. Lake Superior Ports (Iron Age, January 21, 1974) and an iron content in the ore of 51.5%. The estimated new annual costs were \$4,398,000 or 0.069¢ per KWH.

5.2 PRELIMINARY DESIGN AND COST ANALYSIS OF SELECTIVE NO_x REDUCTION WITH AMMONIA SCHEMES

Two selective NO_x reduction with ammonia processes were subjected to preliminary design and cost analysis. One was assumed promoted by a non-noble metal catalyst (e.g., FeCr oxide or V_2O_5) at 399°C (750°F) and 15,000 hr^{-1} space velocity; the other was assumed promoted by platinum at 204°C (400°F) and 20,000 hr^{-1}.

The engineering analysis was based on data generated under Task 2 of this program (Section 4.5). Greater than 90% NO_x reduction was assumed in both cases. An SO_2-free flue gas was assumed for the platinum promoted process. The flue gas composition used for the non-noble metal process is that presented in Table 38, Section 5.1. Anhydrous ammonia was injected to both flue gases at an NH_3-to-NO mole ratio of one (experimental data requirement). However, the reaction

$$4NH_3 + 6NO \rightarrow 5N_2 + 6H_2O$$

requires that the NH_3/NO ratio be 0.67. The excess ammonia was considered lost for the purpose of this analysis (either decomposed or emitted to the atmosphere).

Both processes (non-noble metal and platinum) were adapted to an 800 MW power plant, either existing or new; however, costs for "breaking" into an existing plant were not estimated. The multi-stage catalytic reactor depicted in Figure 26, Section 5.1, was selected for both schemes. A simpler reactor may be preferable for the platinum promoted scheme, e.g. the type used by Environics (Section 3.2.2), but design and cost data on such a reactor were not available.

Heat and mass balance computations, equipment sizing and costing, and operating cost determinations were made as described for the simultaneous NO_x-SO_x reduction processes.

Catalyst replacement was assumed to occur once per year; platinum was assumed reclaimed. Ammonia was priced at 12¢ per pound.

5.2.1 NO_x Reduction by Ammonia on Non-Noble Metal Catalysts - Power Plant Adaptation Scheme

Figure 29 is a schematic flow diagram indicating the adaptation of the selective NO reduction process with ammonia on non-noble metal catalysts to an 800 MW power plant. The power plant flue gas is diverted downstream of the economizer (750°F) to a catalytic reactor where NO_x is reduced to N_2 by ammonia. The virtually NO_x-free flue gas is returned to power plant heat exchangers upstream of the air preheater at a temperature very nearly that at which it was diverted (750°F). Anhydrous ammonia is added to the flue gas upstream of the catalytic reactor; the flue gas is relieved of fly ash by multiclones located upstream of ammonia injection. The process scheme assumed that any SO_x present in the flue gas will go through the catalyst unaffected (experimental data verified this assumption for Fe-Cr oxides and vanadia catalysts).

Table 46 and 47 present summaries for the breakdown of the estimated capital and operating costs for the NO_x removal process. As indicated in Table 47, the cost of anhydrous ammonia accounts for a major portion (68%) of the total operating cost. The relatively high current price of ammonia ($0.12/lb) is in part due to a shortage of supply, and any significant increase in ammonia production should result in a decrease in its price. The data in Tables 46 and 47 indicate estimated total capital and operating costs of $6.15/KW and 0.088¢/KWH, respectively.

Details are given in Tables B-10 and B-12 (Appendix B).

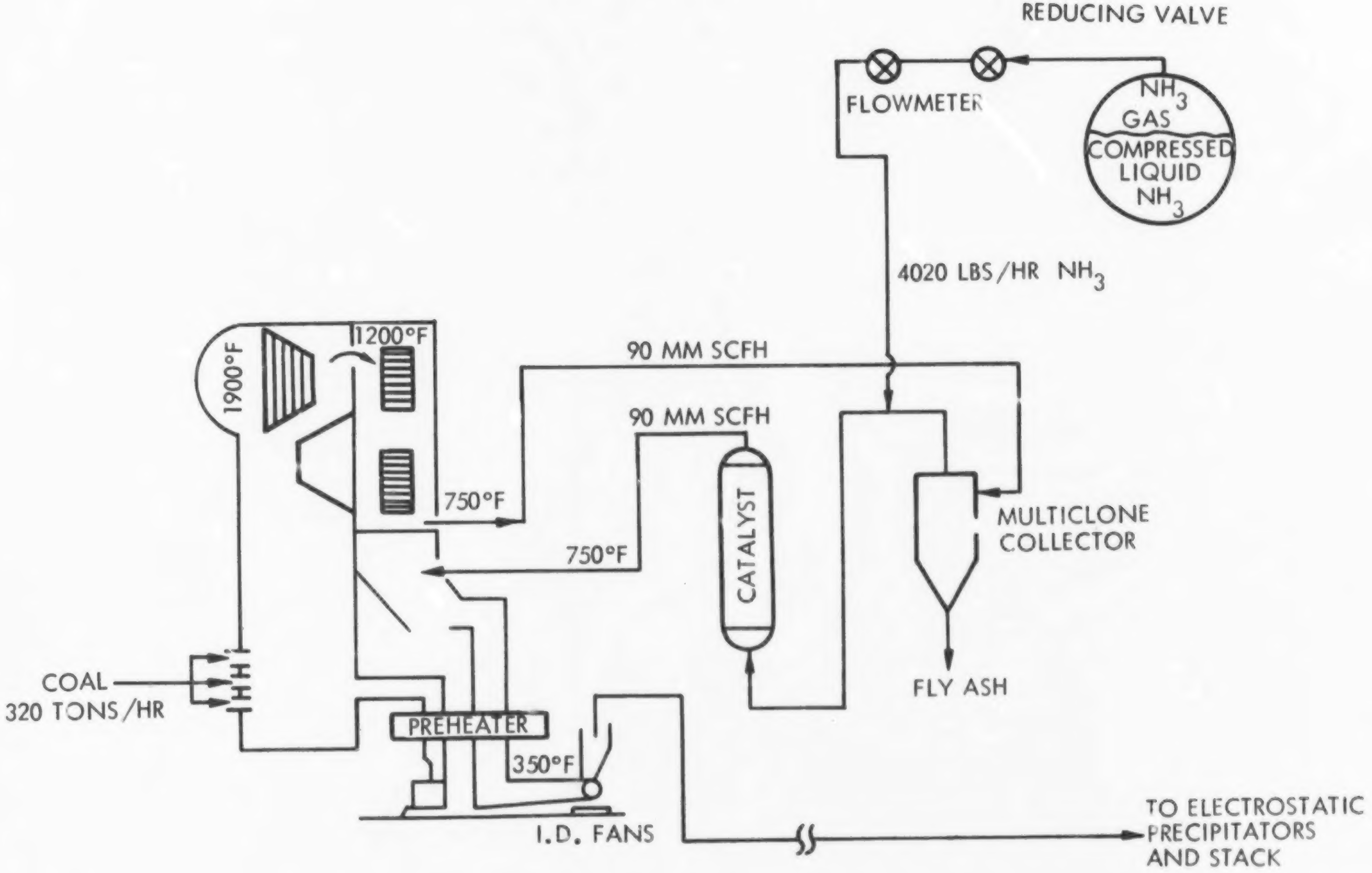
REDUCING VALVE
FLOWMETER
NH3 GAS
COMPRESSED LIQUID NH3
4020 LBS/HR NH3
1200°F
1900°F
90 MM SCFH
90 MM SCFH
750°F
750°F
CATALYST
MULTICLONE COLLECTOR
FLY ASH
COAL
320 TONS/HR
PREHEATER
350°F
I.D. FANS
TO ELECTROSTATIC PRECIPITATORS AND STACK

Figure 29. NO_x Reduction with Ammonia Scheme - (Non-Noble Metal Catalyst)

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Table 46. BREAKDOWN OF THE ESTIMATED CAPITAL COST FOR NO_x REDUCTION BY AMMONIA SCHEME - NON-NOBLE METAL CATALYSTS (Table B-10 in Appendix B presents details)

	Cost ($000)
Ducts	1,685
Multiclones	905
Catalytic reactor	1,505
Ammonia storage tank and feeding system	170
Induced draft fans	650
	4,925
	(or $6.15/KW)

Table 47. SUMMARY OF THE BREAKDOWN OF THE ESTIMATED OPERATING COST FOR NO_x REDUCTION BY AMMONIA SCHEME - NON-NOBLE METAL CATALYSTS

	Cost ($000)
Depreciation	492
Maintenance, insurance, taxes, etc.	394
Labor	160
Electric power	521
Energy losses	17
Catalyst replacement cost	195
Ammonia consumption	3,859
	5,638
	(or 0.088¢ per KWH)

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5.2.2 NO_x Reduction by Ammonia on Platinum Catalysts - Power Plant Adaptation Scheme

Except for a lower operating temperature and the use of a platinum catalyst, this process is essentially identical to the ammonia process (described above) using a non-noble metal catalyst. A schematic flow diagram for the process is shown in Figure 30. The sizing of the catalytic reactor and ammonia feeding equipment and the calculation of ammonia consumption rate were based on laboratory test data (Task 2) which had indicated a maximum NO_x removal efficiency of 91.7% for the following operating conditions: temperature 204°C (400°F); ammonia-to-NO volume ratio 0.977; and space velocity 20,000 hr^{-1}.

Summaries of capital and operating costs for the process are presented in Tables 48 and 49, respectively. Because of the high cost of platinum ($35.55/Kg for a catalyst containing 0.5% platinum by weight), the initial catalyst charge represents a significant capital investment (44,350,000 or 56% of the total capital cost). The processing (rejuvenation) of catalyst was assumed to be on a once-per-year basis at an estimated cost of $11.13/Kg. The data in Table 49 indicate that catalyst restoration and ammonia consumption costs account for 18.4 and 51.2% of the total operating cost, respectively. The total estimated capital and operating costs for the process correspond to $9.64 per KW and 0.115¢ per KWH, respectively. Details are presented in Tables B-11 and B-12 in Appendix B of this report.

5.3 SUMMARY OF PRELIMINARY DESIGN AND COST ANALYSIS RESULTS ON FIVE NO_x ABATEMENT SCHEMES ADAPTED TO 800 MW POWER PLANTS

Table 50 presents a summary of the costs associated with the adaptation of selected simultaneous SO_x-NO_x reduction and selective NO_x reduction with ammonia processes to an 800 MW power plant. This Table also indicates the most cost sensitive items for each scheme.

The five schemes summarized in Table 50 represent three NO_x abatement processes. The NO_x-SO_x simultaneous catalytic reduction process was designed and costed for adaptation to new and existing power plants (800 MW). The simultaneous NO_x-SO_x reduction Sulfide Process (catalytic-throwaway or regenerative) was adapted to new power plants (800 MW). The selective NO_x

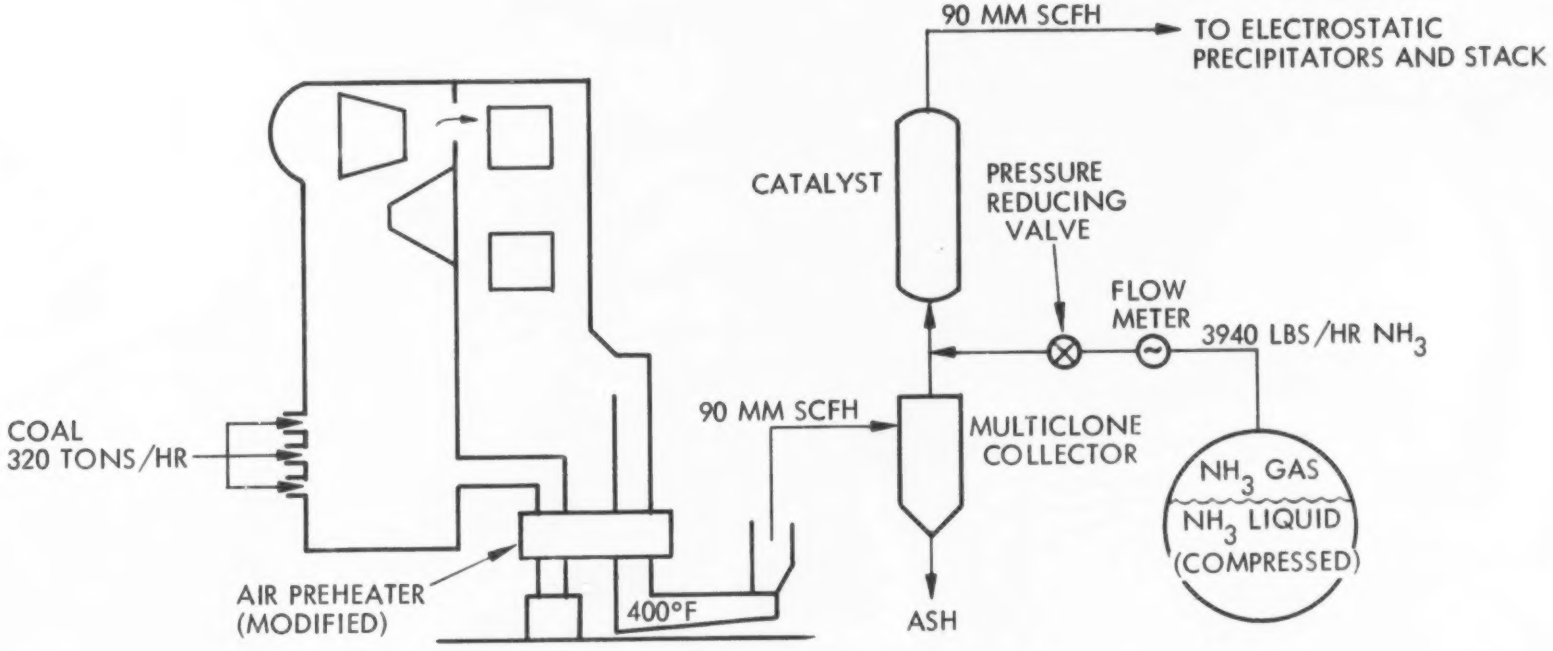
90 MM SCFH
TO ELECTROSTATIC PRECIPITATORS AND STACK
CATALYST
PRESSURE REDUCING VALVE
FLOW METER
3940 LBS/HR NH_3
90 MM SCFH
MULTICLONE COLLECTOR
NH_3 GAS
NH_3 LIQUID (COMPRESSED)
COAL 320 TONS/HR
AIR PREHEATER (MODIFIED)
400°F
ASH

Figure 30. NO_x Reduction with Ammonia Scheme - Platinum Catalyst

Table 48. BREAKDOWN OF THE ESTIMATED CAPITAL COST FOR THE NO_x REDUCTION BY AMMONIA SCHEME - PLATINUM CATALYSTS. (Table B-11 in Appendix B presents details)

	Cost ($000)
Ducts	850
Multiclones	755
Catalytic reactor (including catalyst charge)	5,285
Induced draft fans	650
Ammonia feeding equipment	170
	7,720
	(or $9.64 per KW)

Table 49. BREAKDOWN OF THE ESTIMATED OPERATING COST FOR THE NO_x REDUCTION BY AMMONIA SCHEME - PLATINUM CATALYSTS (Table B-12 in Appendix B presents details)

	Cost ($000)
Depreciation	772
Maintenance, insurance, taxes, etc.	618
Labor	160
Electric power	521
Energy loss	172
Catalyst restoration	1,361
Ammonia consumption	3,782
	7,386
	(or 0.115¢ per KWH)

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Table 50. CAPITAL AND OPERATING COST ESTIMATES FOR THE ADAPTATION OF CATALYTIC NO_x AND NO_x-SO_x SCHEMES TO AN 800 MW POWER PLANT

SUMMARY TABLE[a]

Costs	NO_x-SO_x Cat. Red. Process[b]		Sulfide Process (NO_x-SO_x Reduction) New Plants[d]	NO_x Reduction by Ammonia Process	
	Power Plant New	Power Plant[c] Existing		Non-Noble Metal Catalyst	Noble Metal Catalyst
Capital Cost ($)					
Total	7,305,000	14,935,000	5,075,000	4,925,000	7,720,000
Per KW	9.13	18.67	6.35	6.15	9.64
Operating Cost ($)					
Annual	2,529,000	3,988,000	9,482,000	5,638,000	7,386,000
Per KWH, ¢	0.040	0.062	0.15	0.088	0.115
Major Cost Items	Ducts, Catalytic Reactor	Heat Exchanger, Ducts	Scrap Iron	NH_3	NH_3, Catalyst

[a] Costs do not include working capital and return on investment. Ten year straight-line depreciation was used. Maintenance, insurance, taxes = 8% of capital (annually). Power cost: 1.4¢ per KWH. Catalyst replacement (regeneration of Pt) once per year. Costs based on 1973 prices.

[b] Sulfur-product credit was not taken.

[c] Capital costs of waste-heat boiler and coal used in CO generator were not costed: however, credit for power generated in this unit was not taken either.

[d] Scrap iron was costed at $100 per ton. The iron is not regenerated.

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reduction with ammonia on non-noble metal and platinum catalysts process was adapted to new power plants (800 MW), but the computed costs should very closely relate to scheme adaptation to existing power plants. The ammonia process on platinum was designed for SO_2-free flue gas.

Comparison of costs and scheme simplicity considerations suggest the following process ratings:

- For existing or new power plants fired with sulfur-free fuel, the selective NO_x reduction with ammonia on platinum is indicated.

- For existing power plants fired with sulfur containing fuels, the selective NO_x reduction with ammonia on non-noble metal catalysts is indicated, provided an SO_2 abatement process is available and compatible with the ammonia process; the Fe-Cr oxide catalyst is recommended with a second choice being vanadia.

- For new power plants fired with sulfur containing fuels cost comparison indicates that the preferred process is the simultaneous catalytic NO_x-SO_x reduction process. Scheme simplicity and degree of NO_x-SO_x abatement suggest the sulfide process as the most preferable.

It should be noted that the presented engineering analyses were based on conceptual schemes supported with only a few points of proof-of-principle data; consequently, they represent a first level process design and cost effort. The generated cost estimates should be considered as yardsticks of the relative merit of the five schemes rather than as absolute scheme adaptation costs, even though every effort was made to utilize as accurate information as possible in costing them. Previous experience has indicated that preliminary process cost estimates tend to escalate substantially with process development.

6. RECOMMENDATIONS FOR FURTHER ACTION (TASK 4)

Program Tasks 1 through 3 suggested that catalytic NO_x abatement from power plants should be technically and economically feasible. Our assessment of the data reported in the literature and that generated under this program can be summarized as follows:

- The simplest and probably least expensive means of power plant NO_x abatement would be through NO_x decomposition on platinum, provided 50-60% abatement could be considered adequate. It is not certain, however, that this scheme is adaptable to power plant flue gases containing SO_2.

- For existing power plants operating with sulfur free fuels (virtually SO_2-free flue gas), the selective reduction of NO_x with ammonia on platinum is indicated. Recommendation of this process is based principally on its efficient low temperature operation (air preheater temperatures) which renders simplicity to its adaptation to power plants. It is believed that the Environics Corporation data (pilot plant scale) will verify this assessment.

- For the majority of existing power plants operating with sulfur containing fuels, the selective NO_x reduction with ammonia on non-noble metal catalysts (Fe-Cr oxides, V_2O_5) process appears to be the simplest approach. This assessment presupposes the use of a second process for SO_2 abatement.

  A simultaneous catalytic NO_x-SO_x process is potentially adaptable to this type of plant , but additional bench-scale data is required before the technico-economic feasibility of such a scheme can be considered preferable to a series type of NO_x-SO_x abatement scheme (e.g., selective NO_x reduction followed by SO_x scrubbing). A key question on the catalytic NO_x-SO_x process is the efficiency of the catalyst to simultaneously abate both pollutants in a single-stage reactor (the single point data available to us from NYU are considered promising, but insufficient for efficiency assessment). Additional data are also required in order to establish the efficiency of the TRW scheme (Section 5.1) as applied to existing power plants (reductant generation efficiency at temperatures below 800°C (1472°F), efficiency of homogeneous oxygen reduction at 760°C (1400°F), and efficiency of energy absorption at 538°C [1000°F]). Potentially, the scheme appears promising, but its evaluation was based on extrapolated data and on the assumption of the existence of an efficient single-stage catalyst.

- For new power plants, a simultaneous, nonselective NO_x-SO_x reduction scheme is recommended. In new plant adaptation such a scheme can become an integral part of the plant, instead of an add-on retrofit, and, therefore, it can be much more efficient (Section 5.1) than when adapted to existing plants. The catalytic NO_x-SO_x scheme appears very cost effective, provided a single-stage catalytic reactor proves efficient. The Sulfide Process is simpler, but its demonstrated efficiency with iron must be verified with iron oxide or dolomite to be considered a high ranked candidate process.

- For total pollutant abatement (NO_x-SO_x, Hg, As, Sb, PNA, etc.) from either existing or new power plants, a catalytic oxidative wet scrubbing process may be the desired approach, but additional data is required for even a preliminary assessment of the technico-economic feasibility of such processes.

It should be noted that the above scheme assessment is based on very preliminary data and the ranking of the schemes is tentative. However, every effort was made to utilize data in the individual scheme analyses which closely represents power plant conditions, especially coal fired power plants. Thus, the described schemes are believed to be adaptable to real power plants. Their performance and their impact on the efficiency of the power plant can not be precisely determined at this stage of their development. In general, their impact should not exceed that of SO_2 scrubbers. For example, the selective NO_x reduction processes are similar and yet simpler than the CAT-OX desulfurization process and are expected to be more compatible with and to have less effect on power plant operation than the CAT-OX process. There is greater uncertainty on the impact of the simultaneous NO_x-SO_x reduction schemes on the efficiency of existing power plants. In principle, they should have no impact because they do not require but generate energy which can be tapped independently of the main power plant.

The apparent conditional assessment and ranking of the above NO_x abatement schemes do not imply doubts on the potential of these processes; they merely suggest that additional effort is required before the optimum NO_x abatement scheme(s) for power plant adaptation can be selected. The ensuing paragraphs present the recommended course of action (technical plan) for selection and development of the optimum process or processes and the corresponding adaptation of the scheme(s) to the demonstration-scale level. The recommended program is presented in the following four tasks.

Task 1 - Bench-Scale Development of the NO_x-NH_3-Non-Noble Metal Catalyst Scheme

It is proposed that the iron-chromium oxide catalyst (NA-28) which promoted the oxidation of excess ammonia to the prime choice for this scheme with vanadia as the alternate candidate. It is recommended that 0.5 to 2.0 kilogram catalyst beds be tested on appropriately modified actual flue gas (this size of system is considered to be the most cost effective since it permits the generation of data that can be safely extrapolated without requiring large capital expenditures for experimental set-up).

The following investigations are recommended as a minimum effort for this task:

- Determination of process parametric effects (S.V., temperature, oxygen, water vapor, nitric oxide concentration, NH_3/NO ratio, SO_2). These parameters are to be investigated for quantitative data generation in the range of process operability determined in this phase of the program.
- Development of empirical NO_x reduction rate expressions.
- Generation of process design curves adequate for pilot or demonstration plant engineering design.
- Update of engineering analysis performed in this program phase.
- Determination of long-term catalyst stability (at least 200 hours of operation with a single batch of catalyst, which should include several temperature and environment cycles).
- Assessment of current nonregulated emissions resulting from NO_x catalyst schemes.
- Total power plant impact of NO_x control: i.e., cost, effluent changes, temperature effects, and effects on current emissions control equipment efficiency, durability, and operating costs.
- Projected demand, cost, and availability of the active catalyst materials.

Task 2 - Bench-Scale Development of a Simultaneous Nonselective NO_x-SO_x Reduction Scheme

It is recommended that the objective of this task be the investigation of the sulfide process and the catalytic NO_x-SO_x process for both new and existing power plants on a single bench-scale set up. The task is comprised of two major subtasks. The first subtask involves the investigation of the sulfide process as well as reductant generation for the catalytic NO_x-SO_x process. The second subtask involves parametric investigations on the most promising nonselective NO_x-SO_x reduction catalyst (e.g., the NYU catalyst).

It is proposed that the first subtask involves the following investigations:

- Proof-of-principle tests on iron oxide or dolomite utilization in the sulfide process.
- Proof-of-principle tests on iron oxide or dolomite (calcium-magnesium oxide) regeneration.
- Determination of parametric effects on coal gasifier operated as a reductant generator for the catalytic NO_x-SO_x processes and as a sulfide process reactor.
- Determination of reductant generation rates for new power plants (∿1700°F) and for existing power plants (∿1400°F).
- Determination of iron oxide or dolomite consumption and regeneration rates for efficient NO_x-SO_x abatement (if proof-of-principle tests prove successful).
- Determination of homogeneous oxygen reduction rates at 1700 and 1400°F (927 and 760°C) in simulated boiler (catalytic NO_x-SO_x processes). Determination of excess reductant oxidation by air in boiler (sulfide process).

- Update of engineering analysis on sulfide process (if proof-of-principle tests on iron oxide or dolomite prove successful).

- Determination of long-term recyclability of iron oxide or dolomite (at least one ten cycle test).

The effort in the second subtask should involve the following:

- Determination of optimum operating conditions for selected NO_x-SO_x catalyst through parametric investigations.

- Determination of empirical rate expressions for NO_x-SO_x reduction.

- Update of engineering analyses on the nonselective catalytic NO_x-SO_x schemes (existing and new power plants).

- Determination of long-term catalyst stability (at least 200 hours of operation with a single batch of catalyst, which should include several temperature and environment cycles).

Task 3 - Nitric Oxide Decomposition on Platinum

This task may be investigated as an extention of Task 1; therefore, the same experimental apparatus can be used for both tasks. Three month schedule at a 0.5 man year level should be sufficient for this task, if performed in conjunction with Task 1. The recommended effort should involve the investigation of the SO_2 effect on catalytic activity, the effect of NO_x and oxygen concentrations on decomposition rates, and long term catalyst stability tests.

Task 4 - Proof-of-Principle Tests and Preliminary Engineering Analysis on Total Pollutant Abatement Scheme (TRW OXNOX Process)

Proof-of-principle tests on this process should involve: (a) catalytic oxidation of NO to NO_2 at low space velocities and temperatures, and (b) total pollutant process scrubbing efficiency. In addition, a preliminary engineering analysis, similar to those presented in Section 5, should be performed on this process.

The effort is estimated at the one man year level with a six month schedule.

The proposed program recommends the bench pilot scale development of more than one NO_x abatement process. The rationale behind the multi-process recommendation is predicted on the following:

- Nitric oxide abatement requirements on existing power plants vary because of fuel used, geographical location, SO_2 abatement schemes used or expected to be used. Thus, a single NO_x abatement process is not expected to be universally desirable or even acceptable. Reductant availability and cost, grounds availability, and power plant design are additional variables that can influence selection of the desirable NO_x abatement scheme. Thus, more than one scheme should be available for existing power plants.

- Nitric oxide abatement schemes for new power plants should be integrable with other pollutant abatement schemes, preferably into a single unit. Since SO_2 is the other major pollutant emitted by power plants, a process that simultaneously and efficiently controls both pollutants must be developed for these plants. With existing power plants, the integrated approach to air pollution control is not easy or may not be possible; with new power plants it appears feasible (at least for NO_x-SO_x abatement). Ideally, simultaneous total pollutant abatement is desirable.

- Near term and distant solutions to NO_x pollution may differ. Development of proven feasible NO_x abatement processes should not be reason for discontinuing proof-of-principle tests on potential total pollutant abatement processes to be used as a second generation approaches.

APPENDICES

APPENDIX A

PARAMETRIC EFFECTS ON N_2O PRODUCTION DURING NITRIC OXIDE REDUCTION WITH AMMONIA ON PLATINUM CATALYSTS

A number of tests were performed to investigate the effect of NH_3 and oxygen concentrations and the NH_3-to-NO ratio on N_2O production during NO reduction with ammonia on platinum catalysts. Several tests were performed with a helium carrier in order to obtain a meaningful nitrogen mass balance. The N_2O, O_2, and N_2 flue gas components were monitored chromatographically in these tests (Porapak Q and molecular sieve 5A columns at 25°C).

Table A-1 summarizes the data taken on the NA-1 catalyst (0.5% Pt on alumina). It is noted in the table that the obtained nitrogen mass balance (columns 16 and 17) is as good as can be expected from the analytical instruments used and the number of species (NO, NO_2, N_2O, NH_3, N_2) and quantities involved.

The first four experiments in Table A-1 were performed using typical, sulfur free, simulated flue gas containing 14% CO_2, 5% H_2O, and 3% oxygen by volume. The utilized ratios appear in column 5 and lie on both sides of stoichiometry (the value of the ratio at stoichiometry is 0.667) for the desired reaction

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (1A)$$

AT 250°C (Experiments Nos. 3 and 4) N_2O production was substantial, regardless of NH_3 to NO ratio in the feed flue gas; however, the quantity of N_2O produced doubled when this ratio was increased from 0.482 (∿40% below stoichiometry) to 1.02 (∿20% above stoichiometry). Since NO conversion (3rd column from the right) increased only by 30%, it is assumed that at least some of the N_2O produced is the result of ammonia oxidation by oxygen. According to the literature, ammonia oxidizes to NO on noble metal catalysts at temperatures above 300°C and to N_2O at lower temperatures. Experiment Nos. 3 and 4 indicate that NH_3 concentration had a large effect on N_2O production in the presence of oxygen; thus, complete process selectivity toward Reaction 1A was not verified.

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Table A-1. PARAMETRIC EFFECTS ON N_2O PRODUCTION ON $Pt-Al_2O_3$ (NA-1)

		Reactor Feed Gas Composition							Monitored Reactor Outlet					Total System Nitrogen Balance, ppm				
Exp. No.	Catalyst Temp. °C	NO (ppm)	NH_3 (ppm)	NH_3/NO [a]	O_2 (ppm)	H_2O (%)	CO_2 (%)	Diluent Used	NO (ppm)	NH_3 (ppm)	N_2O (ppm)	N_2 [b] (ppm)	O_2 (ppm)	In	Out	NO Conv. (%)	$\Delta N_2/\Delta NO$ [c]	$\Delta NH_3/\Delta NO$ [d]
	A. EFFECT OF NH_3 CONCENTRATION																	
1	345	1027	120	.117	30,000	5	14	N_2	673	0	50	N.A.	N.A.	N.A.	N.A.	33	N.A.	.27
2	345	982	473	.482	30,000	5	14	N_2	600	60	285	N.A.	N.A.	N.A.	N.A.	39	N.A.	1.08
3	250	982	473	.482	30,000	5	14	N_2	391	N.A.	420	N.A.	N.A.	N.A.	N.A.	60	N.A.	N.A.
4	250	982	1000	1.02	30,000	5	14	N_2	218	N.A.	850	N.A.	N.A.	N.A.	N.A.	78	N.A.	N.A.
5	245	934	3000	3.2	50	0	0	He	0	>3000	0	735	N.A.	N.A.	N.A.	100	.79	N.A.
6	250	1070	1742	1.63	50	0	0	He	0	980	0	810	N.A.	2812	2600	100	.76	.71
7	250	1090	1420	1.30	50	0	0	He	0	657	0	890	N.A.	2510	2437	100	.82	.70
8	250	980	1284	1.31	50	0	0	He	0	393	0	855	N.A.	2264	2103	100	.87	.91
9	250	1000	799	.799	50	0	0	He	0	42	80	690	N.A.	1799	1582	100	.69	.76
10	250	980	564	.576	45	0	0	He	18	40	240	365	130	1544	1268	98	.37	.54
11	250	940	558	.594	50	0	0	He	0	22	279	495?	N.A.	1498	1570?	100	.53	.57
12	250	965	385	.399	50	0	0	He	312	0	235	195	N.A.	1350	1172	68	.30	.59
	B. EFFECT OF OXYGEN CONCENTRATION																	
13	268	994	1170	1.18	70	0	0	He	0	195	0	820	130	2166	1835	100	.82	.98
14	253	918	1050	1.14	80	0	0	He	0	191	0	740	170	1968	1671	100	.81	.94
15	250	918	1019	1.11	630	0	0	He	115	59	710	75	230	1937	1744	87	.09	1.20
16	250	918	1050	1.14	780	0	0	He	131	39	715	100	440	1968	1800	86	.13	1.28
17	250	918	1043	1.14	6250	0	0	He	150	33	560	230	5,800	1961	1763	84	.30	1.07
18	250	918	1104	1.20	10,510	0	0	He	140	42	560	175	10,100	2022	1652	85	.22	1.13

[a] Ammonia to nitric oxide mole ratio in the feed; the stoichiometric value of this ratio for the desired reaction ($6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O$) is 0.667.

[b] Concentration of nitrogen produced during the catalytic reduction of NO with NH_3.

[c] Mole ratio of nitrogen produced to nitric oxide consumed (experimental value).

[d] Mole ratio of ammonia consumed to nitric oxide consumed; the theoretical value of this ratio for the above reaction is 0.667.

In order to isolate the NH_3 concentration effect from that of oxygen, Experiment Nos. 5 through 12 were performed in which the NH_3 to NO mole ratio in the catalyst feed was varied from >3.2 to 0.399. In addition, helium was used as the diluent gas instead of nitrogen; thus, the quantity of nitrogen produced from the reduction of NO was determined. It is apparent that in the absence of oxygen, N_2O production decreased with increase in the NH_3 concentration of the feed, all other parameters remaining constant, while nitrogen production increased. These observations are illustrated in Figure A-1. The exact shape of the curves may not be those drawn, due to data scatter, but the trends are real.

The data from Experiment Nos. 5 through 8 verified Reaction 1A above, when ammonia concentration in the feed stream was equal to or exceeded stoichiometry and oxygen was not present. This is evident from the values of the two ratios tabulated in the last two columns of Table A-1. Within experimental uncertainty, the values of these ratios corresponded to those expected from Reaction 1A. The theoretical values for $\Delta N_2/\Delta NO$ and $\Delta NH_3/\Delta NO$ are 0.833 and 0.677, respectively. When the NH_3 to NO ratio in the catalysts feed dropped below stoichiometry (Experiment Nos. 9 through 12), the ratios in the last two columns of Table A-1 were reduced in value, indicating a different overall reduction reaction than that represented by Reaction 1A. Two reactions that may take place during substoichiometric operation of the process are:

$$4NO + 2NH_3 \rightarrow N_2O + 2N_2 + 3H_2O \qquad (2A)$$

and

$$8NO + 2NH_3 \rightarrow 5N_2O + 3H_2O \qquad (3A)$$

Thus, Experiment Nos. 5 through 12 indicate the following:

- In the absence of oxygen and water vapor Reaction 1A accurately represents the reduction of NO by NH_3 on Pt at 250°C provided at least stoichiometric amounts of NH_3 are present.

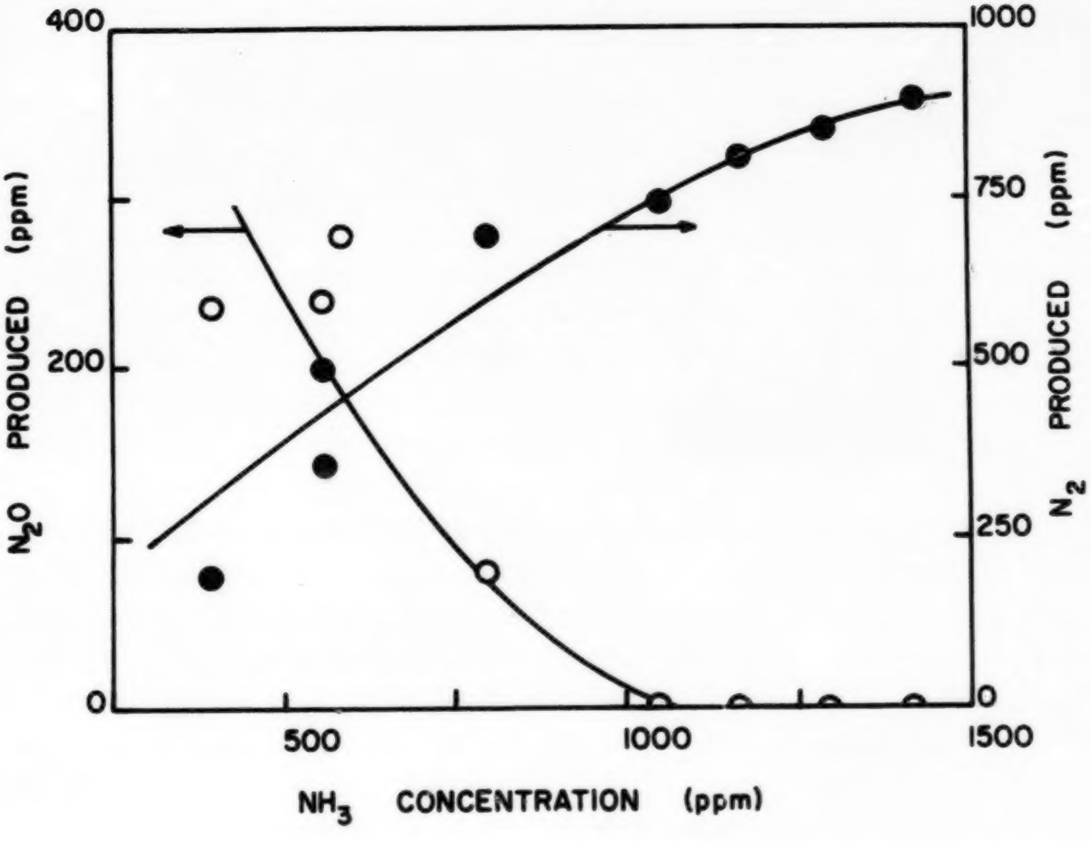

Figure A-1. Effect of NH_3 Concentration on N_2O and N_2 Production. 0.5% Pt on Alumina Catalyst, 1000 ppm NO (nom) in He, 20,000 hr^{-1} (STP), 250-268°C.

- When substoichometric quantities of NH_3 are present in the catalyst feed stream (to as low as 40% below stoichiometry), NO reduction remains near 100% and part of the NO is reduced to N_2O.

- The nitrous oxide, N_2O, is not significant in the catalyst effluent when NH_3 in the feed exceeds stoichiometry, in the absence of O_2, and NO conversion is complete.

Experiment Nos. 14 through 18 were performed in order to more quantitatively determine the oxygen effect. The reactor (catalyst) temperature was kept at 250°C, space velocity at 20,000 hr^{-1} (STP), and the feed NH_3 to NO ratio nearly constant at approximately 60% above sotichiometry (1.11 to 1.20). The oxygen concentration was varied from 0 to 10,000 ppm (1%).

The data from Experiment No. 14 (80 ppm oxygen in the feed gas) indicates compliance with Reaction 1A. Thus, N_2O production is zero, N_2 production is very near to the expected value, and the ΔN_2 to ΔNO ratios are close to the theoretical values. The only discrepancy appears in the ΔNH_3 to ΔNO ratio which is about 20% higher than expected. No explanation is available for this discrepancy. In Experiment No. 15, the oxygen level in the feed gas was raised by approximately one order of magnitude (from 80 to 630 ppm). The data indicated a dramatic oxygen effect on NO reduction. N_2O production increased from 0 to 710 ppm, N_2 production decreased from 740 to 75 ppm, NO conversion decreased from 100 to 87%, the ΔN_2 to ΔNO ratio value was reduced to 0.09 from 0.81, and the ΔNH_3 to ΔNO ratio reached 1.20 from 0.94. The change in the last quantity indicates excess NH_3 utilization which can only be explained through oxygen oxidation. One possible reaction is

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (4A)$$

Reaction 4A apparently takes place in parallel to Reactions 1A, 2A, or 3A, above. It is possible that other reactions, not postulated here, take place. However, whatever the reactions and reaction mechanisms, the fact remains that under the conditions of described experiments, the presence of oxygen in the flue gas at a concentration of at least 630 ppm, influences both the extent of NO conversion and catalyst selectivity. According to the data from Experiment Nos. 16 through 18, the oxygen effect levels off at higher than 630 ppm oxygen concentration in the feed (within experimental uncertainty).

The fact that introduction of O_2 into the test gas mixtures caused a decrease in the conversion of NO was somewhat disturbing in view of reports in the literature that O_2 enhances the reduction of NO with NH_3 on Pt (Section 3.2.2). In addition, the tests conducted had not determined that an NO conversion maximum exists. Additional tests were performed with variable O_2 concentration over a wider range in temperatures using a second sample of $Pt\text{-}Al_2O_3$ catalyst (NA-2).

Table A-2 shows the results of a series of experiments in which CO_2 and H_2O were not incorporated in the test gas mixture. Oxygen concentration was varied from 0 to 3000 ppm.

As before complete conversion of NO occurred with about 1100 ppm NH_3 in the absence of O_2 at about 250° (see Runs 10 and 11 in this table and Run 8 in Table A-1). Very little N_2O was produced with excess NH_3 in the absence of O_2 as described before.

Figure A-2 shows the effect of temperature on conversion and N_2O production more clearly. The reason for the discrepancy between reported enhancement and the observed retardation by O_2 at 250°C, as indicated earlier, is now apparent. Above 220°C O_2 indeed has a retarding effect while below 220°C the effect is one of enhancement. The effect of O_2 on N_2O production is quite pronounced in the 0-800 ppm range; however, there appears to be little influence due to O_2 concentration between 800 and 3000 ppm on either NO conversion or N_2O production. In fact, at 250°C, the conversion indicated for the O_2 tests is in close agreement with that obtained earlier (Table A-1, Run 4) for tests that included CO_2 and H_2O in the mixture, indicating that neither of these constituents is particularly influential to the selective NO reduction by ammonia.

Table A-2. EFFECT OF O_2 ON REDUCTION OF NO WITH NH_3 ON Pt-Al_2O_3 (NA-2)

Run No.	Temperature (°C)	Inlet Gas Composition (ppm)[a]			Outlet Gas Composition (ppm)			NO Conversion (%)
		NO	O_2	NH_3	NO	N_2O	NH_3	
1	290	1000	3000	1141	200	520	0	80.0
2	260	1000	3000	1141	145	648	0	85.5
3	230	1000	3000	1141	100	764	0	90.0
4	190	1000	3000	1141	75	725	0	92.5
5	167	1000	3000	1141	40	807	0	96.0
6	147	1000	3000	1141	62	657	52	93.8
7	126	1000	3000	1141	468	176	608	53.2
8	125	1000	0	1141	1000	0	1042	0
9	205	1000	0	1141	277	60	735	72.3
10	240	1000	0	1141	25	0	534	97.5
11	285	1000	0	1141	0	N.A.	432	100
12	410	1000	784	1137	360	235	29	64.0
13	256	1000	784	1137	103	671	12	89.7
14	195	1000	784	1137	65	823	14	93.5
15	178	1000	784	1137	92	756	48	90.8
16	162	1000	784	1137	123	613	98	87.7

[a] Only NO, O_2 and N_2 carrier gas were present. Space velocity ~20,000 hr^{-1}.

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1000 ppm NO; 1140 ppm NH_3 in N_2; 20,000 hr^{-1} (STP) space velocity;

○ ● Without O_2
□ ■ 3000 ppm O_2
△ ▲ 784 ppm O_2
▽ ▼ Data taken with 3% O_2, 5% H_2O, 14% CO_2 also present

Dotted line denotes maximum possible N_2O due to NO-NH_3 reaction alone.

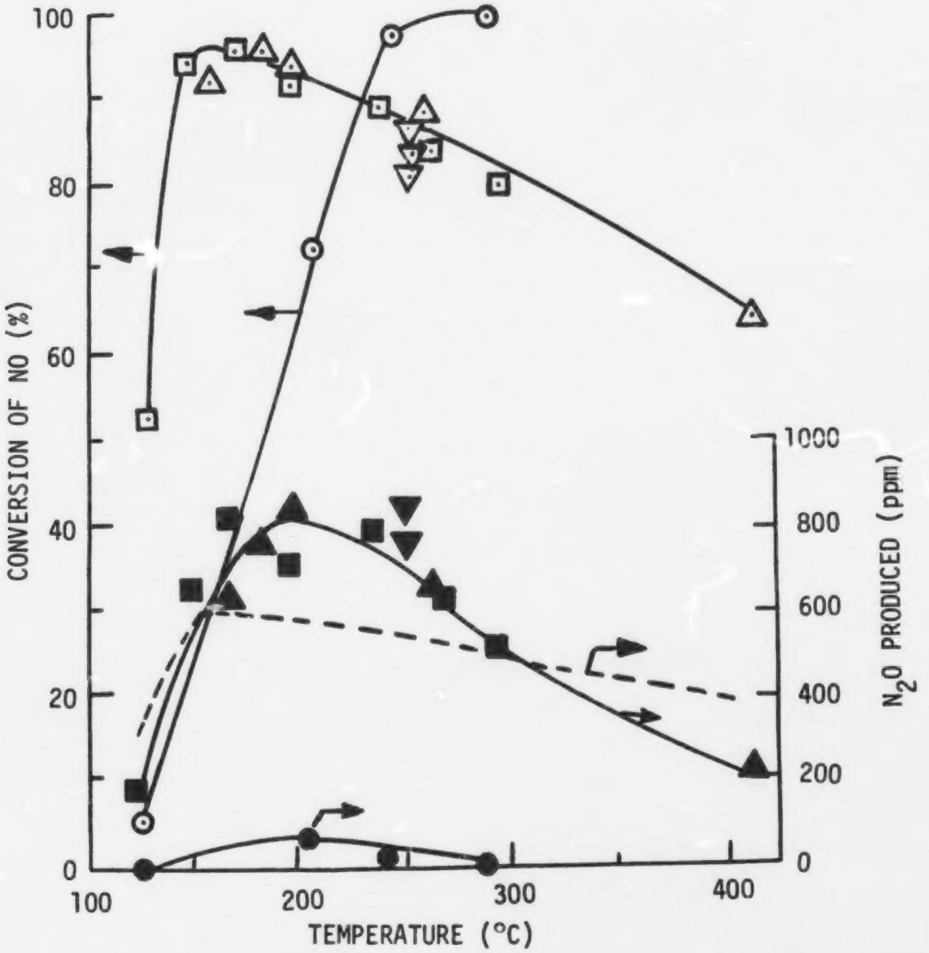

Figure A-2. Effect of O_2 on Selective Reduction of NO with NH_3 and Production of N_2O on Pt-Al_2O_3 (NA-2)

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Up to the temperature for which a maximum in NO conversion occurred in the presence of O_2, the N_2O produced corresponds closely with the maximum possible due to Reaction 3A alone, based on NO conversion observed (as shown by the dotted line in Figure A-2). Above that point N_2O must be a product of the reaction between NH_3 and O_2.

The type of data taken in this project cannot be used to draw mechanistic conclusions for either the relative participation of NO and NH_3 in the formation of N_2O or the shift in the NO conversion curve to lower temperatures in the presence of O_2. Studies to determine such mechanisms, perhaps through the use of isotope labelling, are highly recommended.

APPENDIX B

Table B-1. PARTIAL LISTING OF CONTACTED EQUIPMENT MANUFACTURERS AND SUPPLIERS (Contact was made with the local representatives and/or engineering personnel at the headquarters)

Fans and Motors
- Buffalo Forge Company
- Zurn Air Systems Divsion
- Westinghouse Electric Corporation
- Aerovent, Inc.
- Garden City Fans and Blower Company
- General Electric Company

Refractory Lining and Insulation
- Babcock & Wilcox Refractories Division

Catalysts/Chemicals
- The Harshaw Chemical Company, Catalyst Department
- Engelhard Industries Division, Engelhard Minerals and Chemical Corporation
- U.S. Fuel
- USS Agri-Chemicals Division
- Frank Davis Company, Subsidiary of Rockwood Industries
- Bethlehem Steel Corporation

Cyclones
- Western Precipitation Division, Joy Manufacturing Company
- Envirotech, Air Pollution Control Group

Control Damper
- North American Manufacturing
- Zurn Air Systems Division

Feeders and Associated Equipment
- Greenlee Engineering Company
- Wallace and Tiernan Division, Penwalt Corporation
- American Meter Company, A Division of Singer

Heat Exchanger ("Preheater")
- Bigelow-Liptak Corporation
- Air Preheater Company

Electric Rates
- Southern California Edison Company

CO Generator Vessel, Chemical Storage Tanks and Duct Material
- Peabody Engineering and Supply Company
- Buffalo Tank Division, Bethlehem Steel Corporation
- American Bridge Division, U. S. Steel
- Chicago Bridge and Iron
- Production Steel

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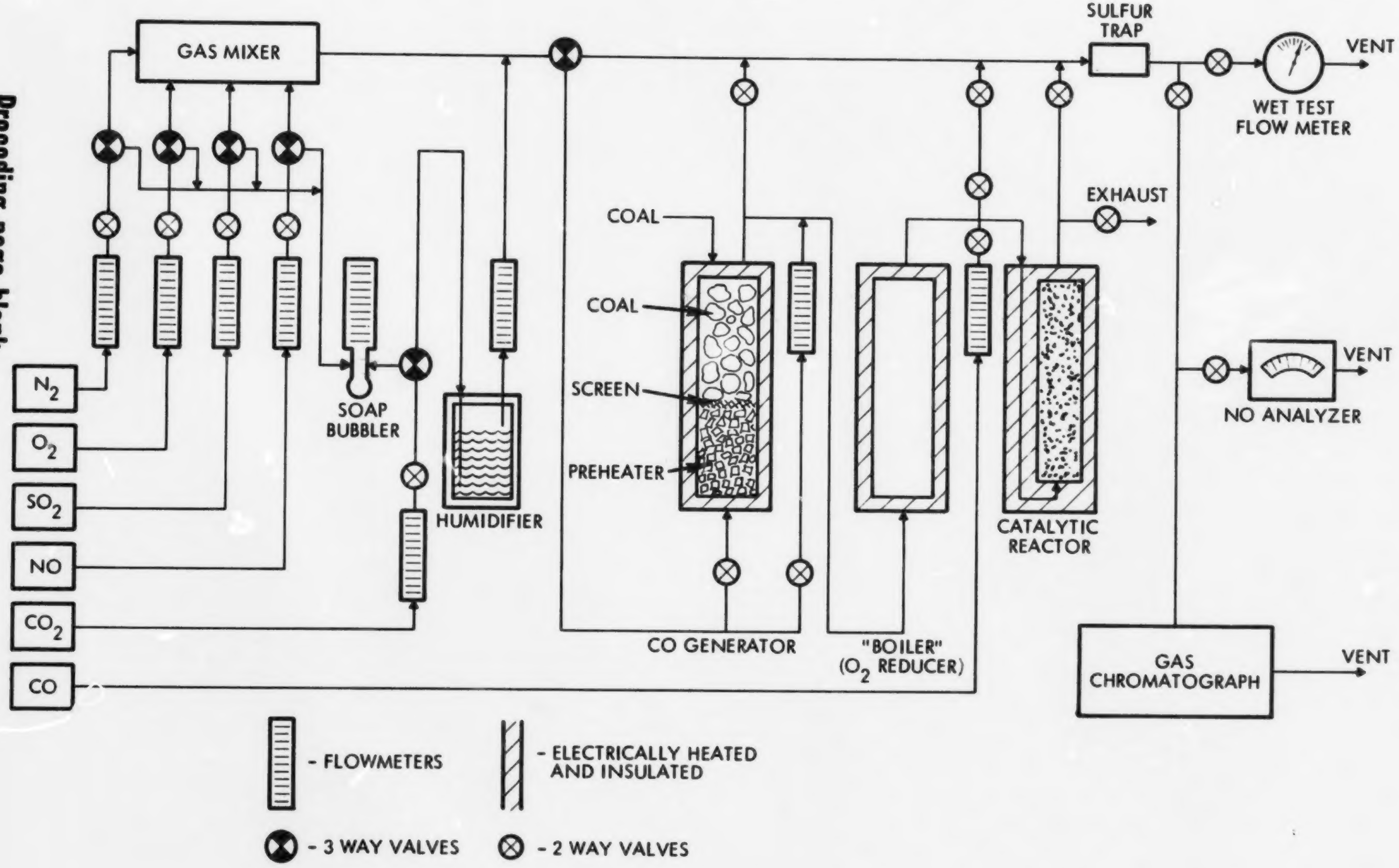
GAS MIXER
SULFUR TRAP
VENT
WET TEST FLOW METER
EXHAUST
VENT
NO ANALYZER
VENT
GAS CHROMATOGRAPH
N_2
O_2
SO_2
NO
CO_2
CO
SOAP BUBBLER
HUMIDIFIER
COAL
COAL
SCREEN
PREHEATER
CO GENERATOR
"BOILER" (O_2 REDUCER)
CATALYTIC REACTOR
- FLOWMETERS
- ELECTRICALLY HEATED AND INSULATED
- 3 WAY VALVES
- 2 WAY VALVES

Figure B-1. Schematic Diagram of Bench Scale NO_x-SO_x Reduction Process Apparatus

Table B-2. SUMMARY OF MASS BALANCE CALCULATIONS FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR NEW POWER PLANTS (37.5% of flue gas diverted to reductant generator at a temperature of 1700°F)

Let a = coal feed rate for CO generator, tons/hr

(320-a) = coal feed rate for primary burners, tons/hr

Flue gas generated at primary burners = (320-a) (281,250 SCFH/ton), SCFH

Flue gas diverted to reductant generator (37.5%) = (320-a) (281,250) (0.375)
= (105,467) (320-a), SCFH
= 278 (320-a) lb-mole/hr

Oxygen in flue gas CO generator feed (3%) = 8.34 (320-a) lb-mole/hr

Reactions in the reductant generator

$$C + 1/2\ O_2 = CO \qquad (1)$$

$$2\ (-H) + 1/2\ O_2 = H_2O \qquad (2)$$

$$C + H_2O = CO + H_2 \qquad (3)$$

$$C + CO_2 = 2CO \qquad (4)$$

Moisture content of coal: 4%

Total hydrogen and total oxygen content of coal 5 and 10% respectively

Non-water hydrogen: 5 - 4 (2/18) = 4.6%

Non-water oxygen: 10 - 4 (16/18) = 6.4%

Non-water hydrogen in coal available for reaction (2):

$$\frac{\text{(a tons/hr) (2000 lbs/ton) (0.046)}}{2} = 46\text{ a lb/mole/hr}$$

Non-water oxygen in coal: $\frac{(a)(2000)(0.064)}{32} = 4a$ lb-mole/hr

Assuming oxidation of all the non-water hydrogen, oxygen consumed in reaction (2): $\frac{46a}{2} = 23a$ lb-mole/hr

Flue gas oxygen available for reaction (1): 8.34 (320-a) + 4a - 23a
= (2667 - 27.33a) lb-mole/hr

At 1700°F, contributions from reactions 1, 3, and 4 to the total CO production are 45, 29 and 26%, respectively. Therefore, for 1 lb-mole of CO produced, 0.45 lb-mole originate from reaction (1), 0.29 lb-mole originate from reaction (3) and 0.26 lb-mole originate from reaction (4). These reactions would consume a total of 0.87 lb-mole of carbon (0.45, 0.29, 0.13 lb-mole in reactions 1, 3 and 4, respectively). The fraction of carbon consumed in reactions (1), (3) and (4) are, therefore 0.517, 0.333, and 0.150, respectively.

Table B-2.(Continued) SUMMARY OF MASS BALANCE CALCULATIONS FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR NEW POWER PLANTS

Carbon consumed in reaction (1): 2(2667-27.33a) lb-mole/hr
= 24(2667-27.33a) lbs/hr
= 0.012 (2667-27.33a) tons/hr

Total coal consumed [70% carbon, 51.7% in reaction (1)]
(88.4 - 0.91a) ton/hr

Coal supplied to reductant generator (a) = coal consumed in reductant generator,
therefore, a = 88.4 - 0.91a
a = 46 tons/hr

Coal feed rate to reductant generator = 46 tons/hr
Coal feed rate to primary burner: 320 - 46 = 274 tons/hr
Carbon in the 46 tons/hr of coal fed to reductant generator = 5367 lb-mole/hr
lb-mole/hr CO produced: $\frac{5367}{0.87}$ = 6168
lb-mole/hr H_2 produced: (6168)(0.29) = 1788
lb-mole/hr oxygen in the undiverted portion (62.5%) of flue gas: 3804
lb-mole/hr SO_2 in the undiverted flue gas (0.2%): 254
lb-mole/hr NO in the undiverted flue gas (0.1%): 127
lb-mole/hr sulfur (H_2S and S) in the CO generator effluent gas:

from undiverted flue gas	152
from coal (50% of sulfur released)	43
Total	195

Assuming 60% elemental sulfur, 40% H_2S, total oxygen consumed in "boiler"
for conversion to SO_2: 234 lb-mole/hr
Amount of SO_2 produced: 195 lb-mole/hr
Total amount of SO_2 to be reduced catalytically: 195 + 254 = 449 lb-mole/hr
CO required for catalytic SO_2 reduction (SO_2+2CO 2CO_2 + 1/n S_n): 898 lb-mole/hr
CO required for catalytic NO reduction (NO + CO CO_2 + 1/2 N_2): 127 lb-mole/hr
"Excess" CO to be oxidized by oxygen in the undiverted flue gas:
6168 - (898 + 127) = 5143 lb-mole/hr
Oxygen required for oxidation of "excess" CO: 2571 lb-mole/hr
Oxygen required for oxidation of H_2: 894 lb-mole/hr
Oxygen required for oxidation of H_2S and S: 234 lb-mole/hr
Total amount of oxygen required = 2571 + 894 + 234: 3699 lb-mole/hr
Total amount of oxygen available: 3804 lb-mole/hr
Excess oxygen: 105 lb-mole/hr

TABLE B-3. DESIGN AND CAPITAL COST DATA FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESSES FOR NEW POWER PLANTS

Item	Description	Est. Cost ($000)	
1. Reductant Generation Section			
a) Diversion Damper	22.5' x 22.5', based on flue gas velocity of 4000 ACFM	250	
b) Coal Feeder	Chain type bucket elevator 130 ft long	15	
c) Reductant Generator Vessels	4 vessels, 30 ft diameter, 15 ft high, containing 7 ft of coal (bed volume based on a space velocity of 1500 V/V/hr	185	
	Field erected from carbon steel sheets (1/4-in thick at bottom and first ring, 3/16-in thick at other places).		
	Expected pressure drop 10 in of water (based on coal particle size of 1/2-in and a porosity of 50%)		
	Insulation and refractory lining: 1 layer of firebrick, 1 layer of insulating brick. (Total material cost $10.40 sq ft)	295	
d) Ductwork	250 ft 30 x 30, 1/4-in carbon steel ($10.20 lb/sq ft $900/ton)	345	
	Internal insulation with 3 in vacuum formed ceramic fiber wool ($6.00/sq ft), 1.5 in mineral wool backing ($0.63/sq ft), abrasion resistance ceramic coating ($.17/sq ft), studs ($0.62/sq ft); total estimated material cost at $7.42	555	
			1,645
2. Catalytic Reaction Section			
a) Ductwork	500 ft, 40' x 40', 1/4-in carbon steel (10.20 lb/sq ft $900/ton)	460	
	Internal insulation (see item 1d above)	740	
b) Multiclones	Eight units, Western Precipitation Type, 12V - 35 sixe 270-15 (quoted fabrication price $482,000)	990	
	External insulation (for estimated external surface area of 3070 sq ft per unit) with 1.5-in 8-15 ceramic fiber blanket (1.90/sq ft), 1-in mineral wool backing ($0.63/sq ft), studs ($1 sq ft); total estimated material cost $3.53/sq ft.	220	
c) Catalytic Reactor	30 ft diameter, 130 ft high, consisting of 13 sections (Monsanto multi-stage design). Monsanto 1965 estimated installed cost $2500/ft of height. Estimated 1973 price based on assumed escalation rate of 6 per year ($3985/ft of height)	820	
	Estimated pressure drop through bed 2 in H_2O		
	External insulation (same as for multiclones - item 2b, above)	120	
	Catalyst charge 570,000 lbs, 1/2-in tablets, 50 porosity, 65 lb/cu ft bulk density, $0.50/lb	285	
	Catalyst depth per section 1 ft (based on space velocity of 9000 V/V/hr)		
			3,635
3. Induced Draft Fans and Motors	Fans, 4 units, each 500,000 cfm capacity; total system standard static pressure of 20 in water (price for Buffalo Forge Fans Model #1780 L39, 885 RPM, 1400 HP, $61,000/fan f.o.b.)	500	
	Motors 4 units (G.E. type K motors, 900 RPM, 1500 HP, $30,000/unit)	250	
			750
4. Sulfur Collection Section			
a) Ductwork	250 ft 25' x 25', 1/4-in carbon steel (10.20 lb/sq ft $900/ton)	285	
	250 ft 30' x 30', 1/4-in carbon steel (10.20 lb/sq ft $900/ton)	345	
b) Multiclones	5 units (same as item 2-b above, no insulation)	620	
c) Forced Draft Fans and Motors	2 units, each capable of handling a volume of 169,000 cfm against pressure of 2 in water (price for Aerovent vaneaxial for Model VW C49B, 727 RPM with 125 HP motor $6,300 per unit)	25	
			1,275
			7,305

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Table B-4. OPERATING COST DATA FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR NEW POWER PLANTS

Item	Description	Est. Cost ($000) Per Year
1. Depreciation	10 year straight line (10% of capital investment per year)	730
2. Maintenance, etc.	Maintenance, insurance, taxes, etc.; estimated at 8% of capital investment per year	584
3. Labor	Labor at $5/hr, 3 operating positions, 100% overhead, 8000 working hours per year	240
4. Electric power	Estimated power consumption 6250 HP, 8000 operating hours per year, 1.4¢/KW-hr (based on Southern California Edison Company schedule A-8 for large electric users)	522
5. Energy losses	Equivalent of 3 tons/hr of coal; (estimate includes allowance for heat loss from insulated surfaces, heat rejected in ash discharged from CO generator and multiclones, and heating value not recovered due to CO consumption in the catalytic reactor); estimated price of coal (70% carbon content) $7/ton	168
6. Catalyst replacement	Catalyst cost $0.50/lb, once per year replacement of 570,000 lbs of catalyst	285
		2,529

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Table B-5. SUMMARY OF MASS BALANCE CALCULATIONS FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR EXISTING POWER PLANTS

Coal feed rate for primary burner = 320 tons/hr

Flue gas generated at primary burner = 90×10^6 MM SCFH

let χ = fraction of flue gas diverted to CO generator

$(1 - \chi)$ = undiverted fraction of flue gas

Y = coal feed rate for CO generator, tons/hr

Carbon feed for reductant generator $= \frac{(Y)(0.70)\ 2000}{12} = 117Y$ lb-mole/hr

Non-water hydrogen in reductant generator feed $= \frac{(Y)(0.046)(2000)}{2} = 46Y$ lb-mole/hr

Non-water oxygen in reductant generator feed $= \frac{(Y)(0.046)(2000)}{32} = 4Y$ lb-mole/hr

Oxygen in flue gas feed for reductant generator $\frac{(90 \times 10^6)(\chi)(0.03)}{379} = 7116\chi$ lb-mole/hr

Reactions in reductant generator and estimated per cent contribution from each reaction to the total CO production:

$C + 1/2\ O_2 = CO$	95%	(1)
$2(-H) + 1/2\ O_2 = H_2O$	-	(2)
$C + H_2O = CO + H_2$	5%	(3)
$C + CO_2 = 2\ CO$	0%	(4)

One lb-mole of C consumed (0.95 lb-mole in reaction 1, 0.05 lb-mole in reaction 3) produces 1 lb-mole of CO (0.95 lb-mole from reaction 1, 0.05 lb-mole from reaction 3)

Oxygen consumed in reaction 2 = $23Y$

Oxygen available for reaction 1 $= 7116\chi - 23Y + 4Y$

$= 7116\chi - 19Y$

Carbon consumed in reaction 1 $= 14{,}232\chi - 38Y$

Carbon consumed in reductant generator $= \frac{1}{0.95}(14{,}232\chi - 38Y) = 14{,}981\chi - 40Y$, therefore

$117Y = 14981\chi - 40Y$ and $Y = 95.4\chi$

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Table B-5. (Continued) SUMMARY OF MASS BALANCE CALCULATIONS FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR EXISTING POWER PLANTS

For total oxygen consumption in reductant generator:

CO produced = 117Y lb-mole/hr

H_2 produced = (117Y)(0.05) = 5.85Y 16-mole/hr

Oxygen-consuming reaction in subsequent gas mixing and catalytic reduction

$$\mathrm{CO} + 1/2\ \mathrm{O_2} \rightarrow \mathrm{CO_2} \qquad (5)$$

$$\mathrm{H_2} + 1/2\ \mathrm{O_2} \rightarrow \mathrm{H_2O} \qquad (6)$$

$$2\mathrm{CO} + \mathrm{SO_2} \rightarrow 2\ \mathrm{CO_2} + 1/n\ \mathrm{S_n} \qquad (7)$$

$$\mathrm{CO} + \mathrm{NO} \rightarrow \mathrm{CO_2} + 1/2\ \mathrm{N_2} \qquad (8)$$

SO_2 content of undiverted flue gas = 474.4 (1-x) lb-mole/hr

NO content of undiverted flue gas = 237.2 (1-x) lb-mole/hr

CO required for SO_2 reduction 948.8 (1-x) lb-mole/hr

CO required for NO reduction 237.2 (1-x) lb-mole/hr

Total CO required for catalytic reduction = 1186 (1-x) lb-mole/hr

CO to be oxidized in reaction 5 = 117Y - 1186 (1-x) lb-mole/hr

Oxygen required for reaction 5 = 58.5Y - 593 (1-x) lb-mole/hr

Oxygen required for reaction 6 = 2.92Y - lb-mole/hr

Total oxygen required for reactions 5 and 6 = 61.42Y - 593 (1-x) lb-mole/hr

Oxygen required = oxygen available

61.42Y - 593 (1-x) = 7116 (1-x)

Y = 125.5 (1-x)

Y = 95.4x (from above), therefore

95.4 x = 125.5 (1-)

x = 0.57

Y = 54 tons/hr

Table B-6. DESIGN AND CAPITAL COST DATA FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR EXISTING POWER PLANTS

Item	Description	Est. Cost ($000)
1. Reductant Generation Section		
a) Multiclones	2 units (see item 2b, Table B-3)	250
b) Coal Feeder	Chain type bucket elevator, 30 ft long	[illegible]
c) Reductant Generator Vessels	4 vessels, 40 ft diameter 15 ft high, containing 7 t of coal (bed volume based on a space velocity of 1500 V/V hr) (see item 1c, Table B-3 for descriptive details); expected pressure drop 10-in of water insulation (see item insulation and item 1c, Table B-3)	455
d) Ductwork	To carry flue gas feed for CO generator, 250 ft 30' x 30 (see item 1d, Table B-3 for descriptive detail)	345
	Internal insulation (see item 1d, Table B-3)	555
		1,910
2. Catalytic Reaction Section		
a) Ductwork	To carry undiverted flue gas to catalyst, 250 ft 20' x 20' (see item 1d, Table B-3)	230
	External insulation (at $3.53 material cost/sq ft - see item 2b, Table B-3)	40
	Ductwork to carry flue gas to waste heat boiler, 250 ft 40 x 40 (see item 1d, Table B-3)	
	Internal insulation (see item 1d, Table B-3)	740
b) Multiclones	5 units (see item 2b, Table B-3)	620
	External insulation (see item 2b, Table B-3)	135
c) Catalytic reactor	30 ft diameter 150 ft high 115 sections (see item 2c, Table B-3)	950
	External insulation (see item 2c, Table B-3)	135
	Catalyst charge, 655,000 lb (see item 2c, Table B-3)	325
	Expected pressure drop through bed 2-in H_2O	
	Depth of bed per section 1 ft (based on space velocity of 9000 V/V/hr)	
		3,635
3. Heat Exchanger	20 units 12' x 22' x 13', containing 528 tubes 4-1/2" O.D. (stainless steel and carbon steel tubes; hot side 1 pass coal side 3 passes)	6,870
	Estimated heat transfer rate 625 MM Btu/hr	
	External insulation (at $3.53 sq ft material cost - see item 2b, Table B-3)	250
		7,120
4. Induced Draft Fans and Motors	5 fans (see item 3, Table B-3)	625
	5 motors (see item 3, Table B-3)	310
		935
5. Sulfur Collection Section		
a) Ductwork	500 30' x 30', no insulation (see item 4a, Table B-3)	690
b) Multiclones	5 units (see item 4b, Table B-3)	620
c) Forced Draft Fans	2 units (see item 4c, Table B-3)	25
		1,335
		14,935

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Table B-7. OPERATING COST DATA FOR THE NO_x-SO_x CATALYTIC REDUCTION PROCESS FOR EXISTING POWER PLANTS

Item	Description	Est. Cost ($000) Per Year
1. Depreciation	10 year straight line (10% of capital)	1,493
2. Maintenance, etc.	Maintenance, insurance, taxes, etc. estimated at 8% of capital per year	1,195
3. Labor	Labor at $5/hr, 3 operating positions, 100% overhead, 8000 working hours per year	240
4. Electric power	Estimate power consumption 7750 HP, 8000 working hours per year; 1.4¢/KW-hr (see item 4, Table B-4)	575
5. Energy losses	Equivalent of 3 tons of coal/hr (see item 5, Table B-4)	168
6. Catalyst	Catalyst cost $0.5/lb, once per year replacement of 655,000 lbs of catalyst	327
		3,998

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Table B-8. DESIGN AND CAPITAL COST DATA FOR THE SULFIDE NO_x - SO_x REDUCTION

Item	Description	Est. Cost ($000)
1. Coal/Iron Feeder	Chain type bucket elevator, 30 ft long	25
2. Reductant Generator Vessels	8 units, 30 ft diameter, 15 ft high, containing 7 ft of coal (see item 1c, Table B-3)	
	Vessel cost	370
	Insulation and refractory lining	590
3. Ductwork	250 ft of 50' x 50' (see item 1d, Table B-3)	
	Duct	575
	Internal insulation	925
	250 ft of 45' x 45' (see item 1d, Table B-3)	
	Duct	515
	Internal insulation	835
4. Multiclones	4 units (see item 2b, Table B-3) no external insulation	495
5. Induced Draft Fans and Motors	4 fans (see item 3, Table B-3)	500
	4 motors (see item 3, Table B-3)	245
		5,075

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Table B-9. OPERATING COST DATA FOR THE SULFIDE NO_x-SO_x REDUCTION SCHEME

Item	Description	Est. Cost ($000) Per Year
1. Depreciation	10 year straight line (10% of capital investment per year)	508
2. Maintenance, etc.	Maintenance, insurance, taxes, etc. (8% of capital investment per year)	406
3. Labor	Labor at $5 per hour, 2 operating positions, 100% overhead, 8000 working hours per year	160
4. Electric power	Estimated power consumption 6000 HP, 8000 operating hours, 1.4¢/KW-hr (based on Southern California Edison Company schedule B-8 for large eletric users)	512
5. Energy losses	Equivalent of 3 tons/hr (see item 6, Table B-4)	168
6. Iron Scraps	14 tons/hr, $69/ton (price for ferrous scrap in Los Angeles, Iron Age, January 24, 1974)	7,728
		9,482

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Table B-10. DESIGN AND CAPITAL COST DATA FOR NO_x ABATEMENT BY REDUCTION WITH NH_3 - NON-NOBLE METAL CATALYSTS

Item	Description	Est. Cost ($000)
1. Ductwork	250 ft 40' x 40' (see item 1d, Table B-3)	460
	Internal insulation with 1.5 in of vacuum formed ceramic fiber ($3.00/sq ft), 1.5-in mineral wool backing ($0.63/s ft), ceramic fiber coating cement ($0.17/ sq ft) and studs $0.62/sq ft); total insulation material $4.42/ sq ft	440
	250 ft 35' x 35' (see item 1d, Table B-3)	400
	Internal insulation (same as above)	385
2. Multiclones	6 units (see item 2b, Table B-3)	745
	External insulation (see item 2b, Table B-3)	160
3. Catalytic Reactor	30 ft diameter 170 ft high, 17 sections, estimated actual pressure drop 2.7-in water, (see item 2c, Table B-3)	1,070
	Catalyst charge 300,000 lbs, 1/2 in tablets, 50% porosity, 65 lb/cu ft bulk density, $0.50/lb, catalyst depth per section 1/2 ft (based on space velocity of 15,000 V/V/Hr)	195
	External insulation (at $3.53/sq ft material cost - see item 2c, Table B-3)	240
4. Ammonia Feeding System		
a) Storage Tank	30 ft diameter spherical tank, 5 day ammonia demand storage capacity (for 250 psi internal pressure), field erected	165
b) Pressure Reducing Valve and Flow Meter	2 in axial flow stainless steel controller 12 in turbine meter (maximum capacity 150,000 cu ft/hr)	5
5. Induced Draft Fans and Motors	5 fans, 500,000 cfm capacity each, total system standard static pressure of 9 in H_2O (prices for Buffalo Forge Model #1780, L-39 705 RPM, 1100 BHP $47,500/unit)	490
	5 motors (GE type K motors, 720 RPM, 1250 HP $28,500 per motor)	170
		4,925

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Table B-11. DESIGN AND CAPITAL COST DATA FOR NO_x ABATEMENT BY REDUCTION WITH NH_3 - PLATINUM CATALYST

Item	Description	Est. Cost ($000)
1. Ductwork	300 ft 35' x 35' (see item 1d, Table B-3)	480
	External insulation at $3.53/sq ft material cost (see item 2c, Table B-3)	370
2. Multiclones	5 units (see item 2b, Table B-3)	620
	External insulation at $3.53/sq ft material cost (see item 2c, Table B-3)	135
3. Catalytic Reactor	30 ft. diameter, 130 ft high, 13 sections estimated actual pressure drop 2.6 in water, (see item 2c, Table B-3)	815
	External insulation at $3.53/sq ft material cost (see item 2c, Table B-3)	120
	Catalyst charge 270,000 lbs, 1/8 in tablets, 50% porosity, 60 lb per cubic ft bulk density, catalyst depth per sectio N1/2 ft (based on space velocity of 20,000 V/V/hr), $35.55 per Kg ($26.20 platinum cost, $9.35 manufacturing cost)	4,350
4. Ammonia Feeding System		
a) Storage Tank	See item 4a, Table B-10	165
b) Pressure Reducing valve and flow meter	See item 4b, Table B-10	5
5. Induced Draft fans and Motors	5 fans (see item 5, Table B-10)	490
	5 motors (see item 5, Table B-10)	170
		7,720

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Table B-12. OPERATING COST DATA FOR NO_x ABATEMENT BY REDUCTION WITH NH_3 - NON-NOBLE METAL AND PLATINUM CATALYSTS

Item	Description	Est. Cost Per Year ($000)	
		Non-Noble Metal Catalyst	Platinum Catalyst
1. Depreciation	10 year straight line (10% of capital investment per year)	492	772
2. Maintenance, etc.	Maintenance, insurance, taxes, etc. (8% of capital investment/year)	394	618
3. Labor	Labor at $5 per hour, 2 operating positions, 100% overhead, 8000 working hours per year	160	160
4. Electric Power	Based on 6250 HP, 1.4¢/KW-hr (see item 4, Table)	521	521
5. Energy Losses	For non-noble metal catalyst; equivalent of 0.3 tons/hr coal For noble metal equivalent of 3.2 tons/hr of coal (it includes energy loss due to gas diversion at 400°F instead of 350°F)	17	172
6. Ammonia Consumption	Non-noble metal catalyst: 4020 lbs/hr NH_3 at 0.12¢/lb, 8000 op. hrs/yr Noble metal catalyst: 3940 lbs/hr NH_3 at 0.12¢/lb, 8000 operating hrs/yr	3,859	3,782
7. Catalyst Replacement	One per year replacement of 390,000 lbs of non-noble metal catalyst (at $0.50/lb) Once per year rejuvenation/replacement of 270,000 lbs of platinum catalyst (at $11.13/Kg)	195	1,361
		5,638	7,386

NOTE: Processing cost is assumed to be equal to the labor cost for manufacture of platinum catalyst plus the cost for an estimated 4% platinum loss per cycle)

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